VOLUMETRIC ANALYSIS

BY THE SAME AUTHOR

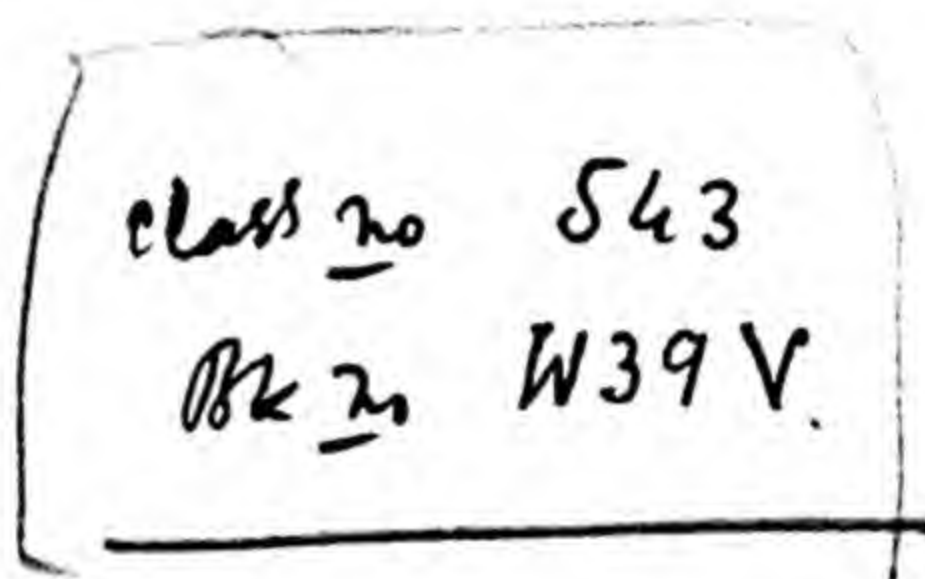CHEMICAL SYMBOLS, FORMULAE AND CALCULATIONS
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VOLUMETRIC ANALYSIS

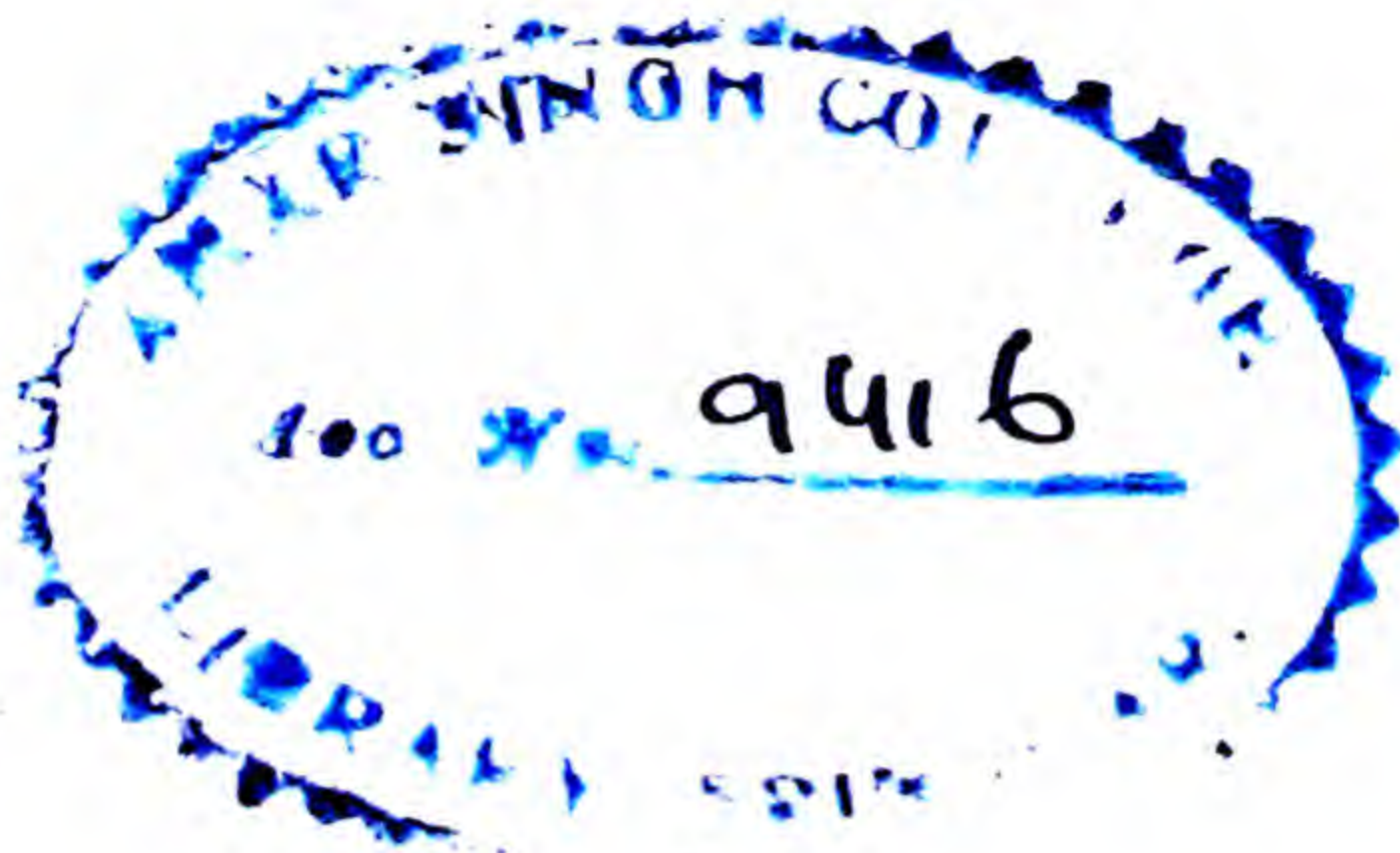## A PRACTICAL COURSE BASED ON MODERN THEORETICAL PRINCIPLES

BY

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DEDICATED
TO THE BOY WHO WROTE
'AN INDICATOR IS A BEAUTIFUL THING'

PREFACE

THIS book is intended to provide a systematic course of practical Volumetric Analysis, not only for junior University students, but for pupils in the higher forms of Secondary Schools. The increasing demands made upon candidates for the Higher School Certificate and University Scholarship examinations make it imperative that the fundamental principles of volumetric methods of analysis should be thoroughly grasped. With this object in view, the subject is treated, wherever possible, from the standpoints of the Ionic hypothesis and the modern Theory of Indicators, and the difference between equivalence and neutrality has been emphasized. A considerable section has been devoted to Iodometry, since this particular branch of volumetric analysis is frequently neglected; iodometric determinations, however, are so simple to perform, and capable of so many applications, that the principles of iodometry should be appreciated by any student of Chemistry. A chapter has been given to the volumetric methods of determining the solubilities of solids, liquids, and gases, an application of volumetric methods which, in the author's opinion, should be emphasized much more strongly than has been the case. A list of suggested experiments has also been added to each chapter, and, finally, a chapter on the modern Theory of Indicators has been included, in which the phenomena due to the hydrolysis of salt solutions are treated from the standpoint of Ostwald's Dilution Law; the subject is thus made more complete by placing it on a mathematical basis.

June 1928

A. W. W.

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VOLUMETRIC ANALYSIS

CHAPTER I

THE GENERAL PRINCIPLES OF VOLUMETRIC ANALYSIS

1. INTRODUCTION. In Volumetric Analysis quantitative determinations are made by means of solutions of accurately known concentrations, and the reagents employed for this purpose must produce certain definite chemical reactions with the substances it is wished to determine. All volumetric determinations involve three distinct steps :

(a) The preparation of the standard reagent ;
(b) The preparation of the solution of the substance to be determined ;
(c) The *titration*, or determination of the volume of standard reagent required to produce a definite reaction with a known volume of the solution to be determined.

The standard solution is prepared either by weighing an exact amount of the reagent, dissolving it, generally, in distilled water, and diluting to a convenient volume ; or by preparing a solution of approximate strength (generally of slightly greater strength than is required), determining the exact strength by special means, and then correcting the approximate solution (generally by diluting it to the desired concentration).

The solution of the substance to be determined is prepared by weighing an exact amount of the substance, dissolving it, and then diluting to a convenient volume. For this purpose a graduated flask is generally employed.

The *titration* is carried out by transferring, by means of a pipette, a measured volume of the test solution to a small flask, and then running in the standard solution from a burette. There are two main methods of determining the end of the reaction :

(i) Where a change occurs in the appearance of the reacting solutions ; e.g. in the titration of a ferrous iron solution with

standard potassium permanganate solution, the 'end-point' of the reaction is denoted when the pink colour of the potassium permanganate just persists. When this point has been reached it is an indication that all the iron in solution has been oxidized from the ferrous to the ferric condition.

(ii) Where a trace of a third substance is added to the reacting solutions to serve as an 'indicator', i.e. a substance which by its change of appearance denotes when one of the reacting solutions is present in a very slight excess; e.g. the use of litmus in titrating strong acids with strong bases.

2. THE ADVANTAGES AND ACCURACY OF VOLUMETRIC METHODS. The volumetric method of analysis, when performed carefully, has important advantages over other quantitative methods. Firstly, there is great economy of time, since a single titration takes only a few minutes; this enables several concordant results to be obtained, and the margin of experimental error is, thereby, reduced considerably. Secondly, it is seldom necessary, when volumetric methods are employed, to separate the products of the reactions, since the presence of comparatively large quantities of other substances has, in general, no effect on the accuracy of a titration.

The accuracy of a volumetric determination does depend, however, upon three factors :

(i) The purity of the reagent in the standard solution ;

(ii) The accuracy of the measuring apparatus—burettes, pipettes, graduated flasks, etc. ;

(iii) The sensitiveness of the indicator, if any, employed in the titration.

It follows, therefore, that a reagent to be employed in making a standard solution must be as pure as possible, and, in any doubtful case, the substance must be repurified before use. The accuracy of the measuring vessels can always be tested (see § 7), and the best indicator for the particular reaction must be chosen in accordance with the rules laid down in §§ 9 and 144.

3. CLASSIFICATION OF METHODS IN VOLUMETRIC ANALYSIS. Although there are isolated methods which cannot be included in any exact classification, volumetric methods have, in general, been divided into three classes. This method of classification is quite arbitrary and is based upon the *type* of

chemical reaction involved in the determination; it is customary to recognize three such distinct types, viz. :

(1) *Methods based upon Acidimetry and Alkalimetry.* This type of volumetric analysis is dealt with in Chapter II.

(2) *Methods based upon Oxidation and Reduction.* Examples of this type are :

(a) The use of potassium permanganate as an oxidizing agent in acid or alkaline solution (see Chapter III).

(b) The use of potassium dichromate as an oxidizing agent in acid solution (see Chapter IV).

(c) The use of iodine, in potassium iodide solution, as an indirect oxidizing agent (see Chapter V).

(3) *Methods based upon Precipitation.* Examples of this type are the uses of (a) a silver nitrate solution in the determination of soluble halides and alkali cyanides ; (b) ammonium thiocyanate solution in the estimation of silver compounds, and in the indirect determination of soluble halides ; (c) sodium chloride solution in the estimation of soluble silver salts (see Chapter VI).

Direct and Indirect Methods

Although the above classification, according to the type of chemical reaction, is general, it is better, perhaps, to divide all methods of volumetric analysis into Direct and Indirect methods.

The Direct Method

In the direct method the determination is the result of a single chemical change in solution. For example :

(a) Methods based upon the equivalence of acids and alkalies, such as the neutralization of sodium hydroxide by hydrochloric acid in aqueous solution :

$$NaOH + HCl = NaCl + H_2O \ ;$$

or, depicting the reaction between the respective ions :

$$NaOH \rightleftharpoons \overset{+}{Na} + \overline{OH}$$

$$HCl \ \rightleftharpoons \overline{Cl} + \overset{+}{H}$$

$$\Updownarrow$$

$$H_2O$$
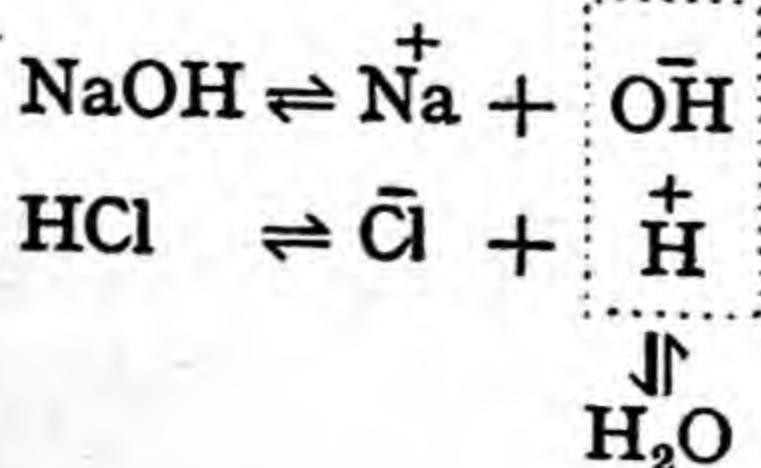
In a similar manner, whenever an acid neutralizes a base, the electropositive hydrogen ions of the acid solution unite quantitatively with the electronegative hydroxyl ions of the base solution to form water, which is only feebly dissociated. We, thus, determine directly the formation of water from its ions.

(b) Simple cases of oxidation with potassium permanganate or potassium dichromate, in acid solution, also come under the heading of direct methods. For example, the oxidation of ferrous sulphate to the ferric condition by means of potassium permanganate, in the presence of sulphuric acid :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O,$$
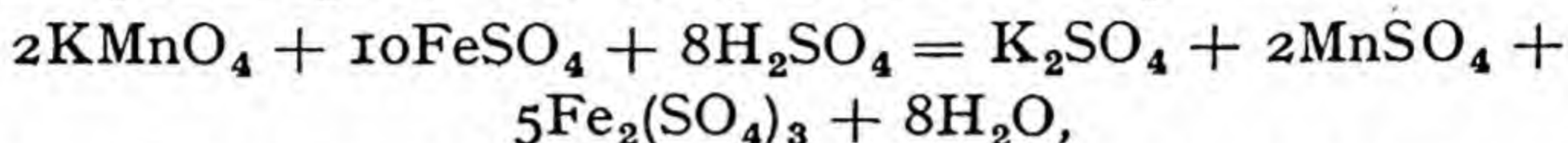
or the oxidation of ferrous chloride to the ferric state by means of potassium dichromate in the presence of hydrochloric acid :

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + Cr_2Cl_6 + 6FeCl_3 + 7H_2O.$$
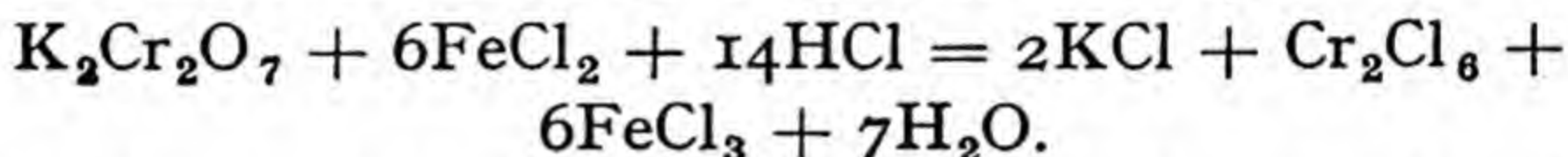
(c) Determinations based upon precipitation often belong to the direct method type of analysis. For example, the determination of sodium chloride in neutral solution by means of silver nitrate solution :

$$NaCl + AgNO_3 = AgCl + HNO_3 ;$$

or, according to the ionic hypothesis :

$$NaCl \rightleftharpoons \overset{+}{Na} + \overline{Cl}$$
$$AgNO_3 \rightleftharpoons \overline{NO_3} + \overset{+}{Ag}$$
$$\Updownarrow$$
$$AgCl$$
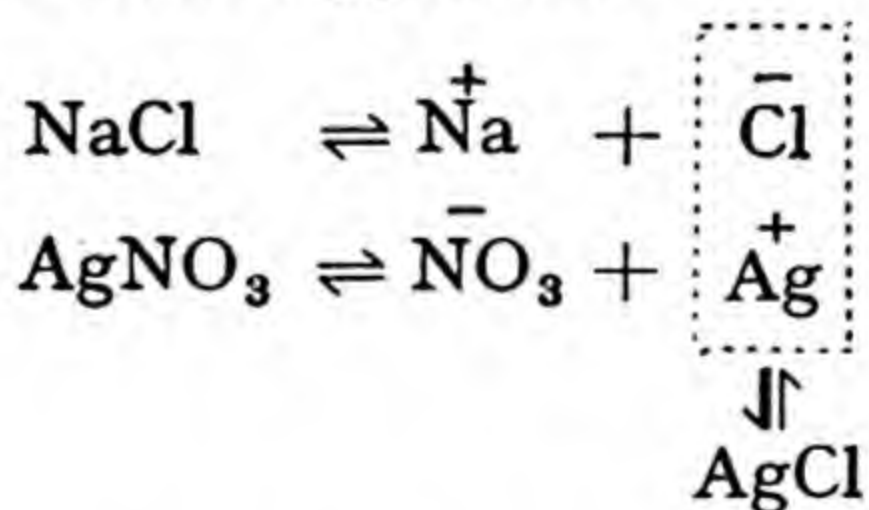
Indirect Methods

Indirect methods may be subdivided into two groups, viz. :

(i) *Determinations in which one, or more, intermediate changes occur.*

For example :

(a) The estimation of peroxides by distillation with concentrated HCl and absorption of the evolved chlorine by excess potassium iodide solution. The iodine liberated in

this reaction is then estimated by titration with standard sodium thiosulphate solution, using starch solution as the indicator. Thus, in the case of manganese peroxide there are three distinct chemical actions :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2,$$
$$Cl_2 + 2KI = 2KCl + I_2,$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$
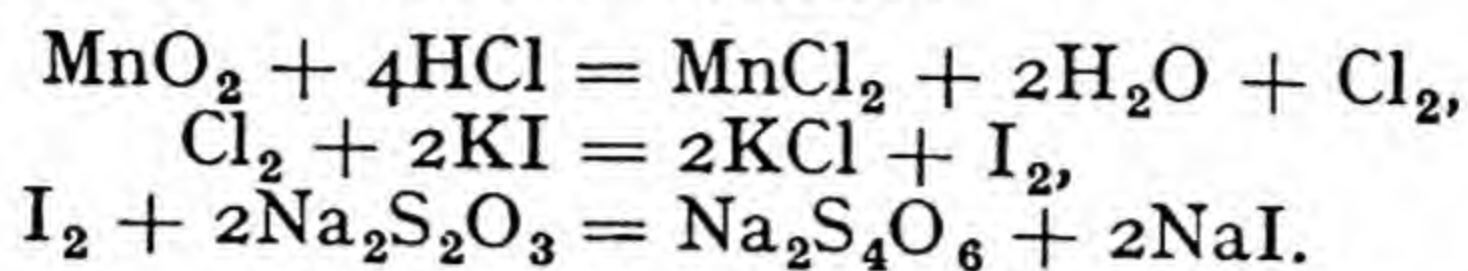
(b) The estimation of ammonium salts by boiling with caustic alkali solution, absorbing the ammonia evolved in a known volume of standard acid, and then determining the excess acid by titration with standard alkali. In the case of ammonium chloride there are thus three separate reactions :

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3,$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4,$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$
(excess)
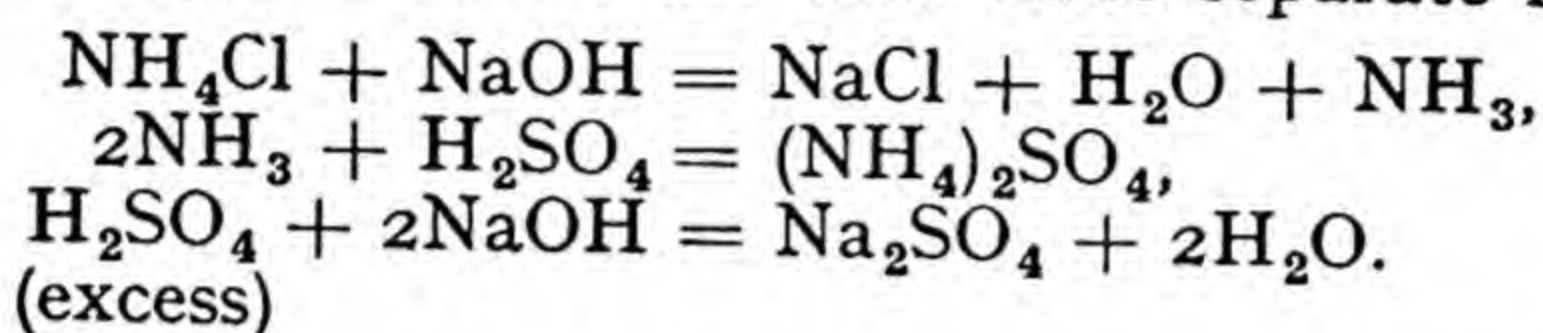
(ii) *Determinations in which the substance to be determined is treated with excess of one standard reagent, and this excess is then determined by titration with a different standard reagent.*

For example :

(a) The estimation of ammonium salts by boiling with a measured excess of standard alkali, and then titrating the residual alkali with standard acid. Thus, in the case of ammonium chloride. we have the two reactions :

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3,$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$
(excess)
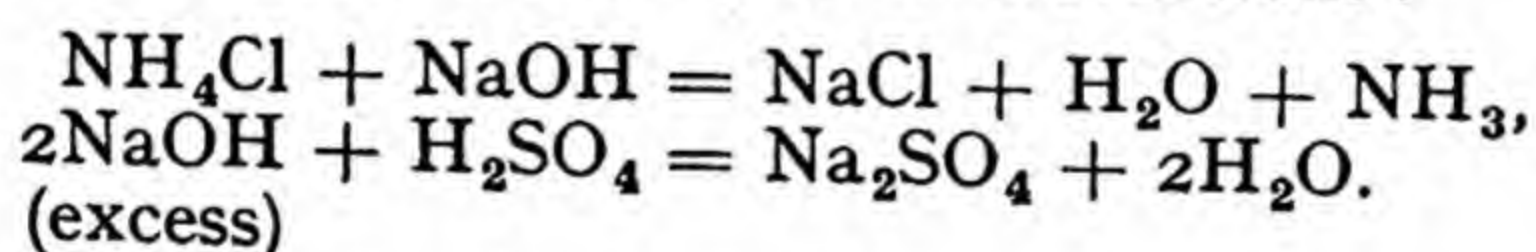
(b) The determination of reducing agents in aqueous solution by adding excess of standard iodine solution, and determining the excess iodine by titration with standard sodium thiosulphate solution. Thus, in the case of hydrogen sulphide in aqueous solution we have the reactions :

$$H_2S + I_2 = 2HI + S,$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$
(excess)
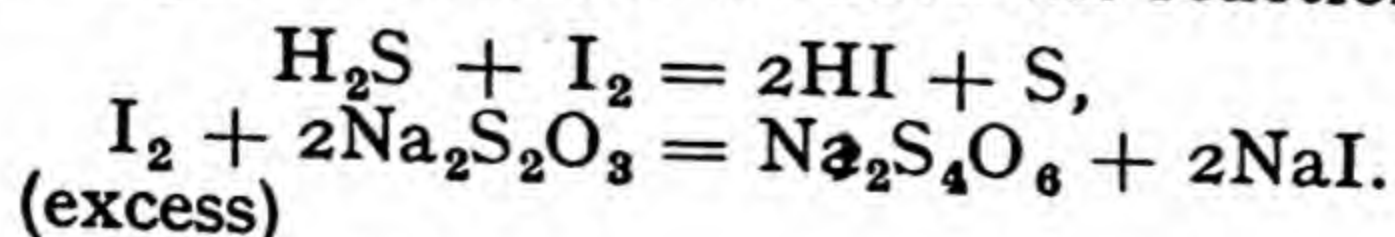
4. STANDARD SOLUTIONS. In volumetric analysis it is necessary to work with standard solutions, i.e. solutions that contain a known weight of reagent in a definite volume of solution. Although a volumetric determination could be performed with solutions containing any known weights of the

necessary reagents, it is much simpler and more efficient to employ solutions of a clearly defined standard strength. The common standard solutions used are *percentage solutions, molar solutions*, and *normal solutions*, and, of these, the last are the most convenient and the most widely used.

Percentage Solutions. The term percentage solution is self-explanatory. For example, a 10 per cent solution of NaCl contains 10 grams of NaCl per 100 grams (or c.c. if the solution is expressed in terms of volume) of the solution.

Molar Solutions. A molar solution is one that contains one gram-molecule of the substance per litre of the solution. For example, a molar solution of hydrochloric acid is one that contains 36·5 grams of pure HCl per litre, and, similarly, a molar solution of sulphuric acid will contain 98·0 grams of H_2SO_4 per litre.

Normal Solutions. A normal solution of any substance contains the gram-equivalent weight of the substance per litre of the solution. By the gram-equivalent weight of the substance is meant the amount of the substance which is equivalent to one gram of hydrogen, i.e. the chemical equivalent of the substance expressed in grams.

For example, *hydrochloric acid* contains 1 gram of ' replaceable ' hydrogen in 36·5 grams of pure HCl, viz. :

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$2 \times 36\cdot5 2$$
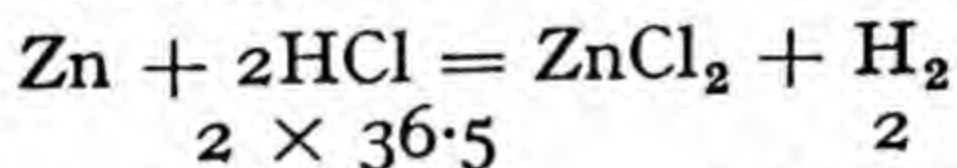
Therefore the chemical equivalent of HCl is 36·5. Thus, a normal solution of HCl contains 36·5 grams of pure HCl per litre. This is exactly the same strength as a molar solution of HCl.

In the same way a normal solution of *nitric acid* is identical with a molar solution, since the molecule of HNO_3 contains one replaceable hydrogen atom.

Sulphuric acid, however, contains two replaceable hydrogen atoms to the molecule, and it follows, therefore, that the chemical equivalent of H_2SO_4 is exactly half the molecular weight of the pure acid, viz. :

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$98 2$$
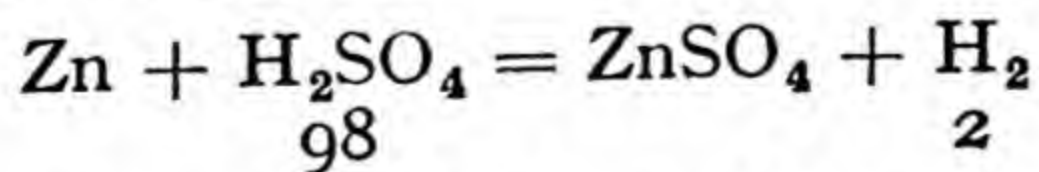
Therefore the chemical equivalent of H_2SO_4 is 49. Thus, a normal solution of sulphuric acid contains 49·0 grams of pure H_2SO_4 per litre, and is equivalent to a semi-molar solution of the same acid.

Acetic acid, $C_2H_4O_2$, which has a structural formula CH_3COOH, contains four hydrogen atoms in the molecule, but only the hydrogen atom in the COOH group is replaceable by metals; therefore a normal solution of acetic acid will also be a molar solution.

Oxalic acid, $C_2H_2O_4.2H_2O$, is dibasic, i.e. both its hydrogen atoms are replaceable by metals; therefore a normal solution of oxalic acid is also a semi-molar solution.

The Chemical Equivalent of a Base

The chemical equivalent of a base is the amount of that base which will neutralize one gram-equivalent of a monobasic acid. For example, since 1 molecule of NaOH will exactly neutralize 1 molecule of HCl, it follows that a normal solution of NaOH is the same as a molar solution. Thus :

$$NaOH + HCl = NaCl + H_2O$$
$$40 \qquad 36.5$$
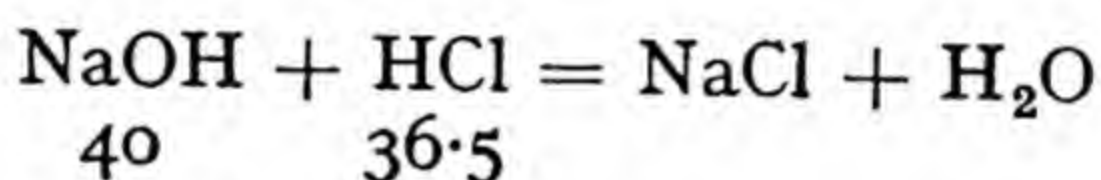
40 grams of $NaOH \equiv^*$ 36.5 grams of $HCl \equiv$ 1 gram of hydrogen; therefore a normal solution of *sodium hydroxide* contains 40 grams of NaOH per litre, and is thus a molar solution.

In the same manner, a normal solution of *potassium hydroxide*, KOH, is also a molar solution, and contains 56 grams of KOH per litre.

A normal solution of *barium hydroxide*, $Ba(OH)_2$, will be equivalent to a semi-molar solution, and will contain 85.5 grams of $Ba(OH)_2$ per litre.

Sodium carbonate, Na_2CO_3, although a salt, is alkaline in solution on account of hydrolysis (see § 9), and, since 1 molecule of the carbonate is equivalent to 2 molecules of a monobasic acid,

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O,$$
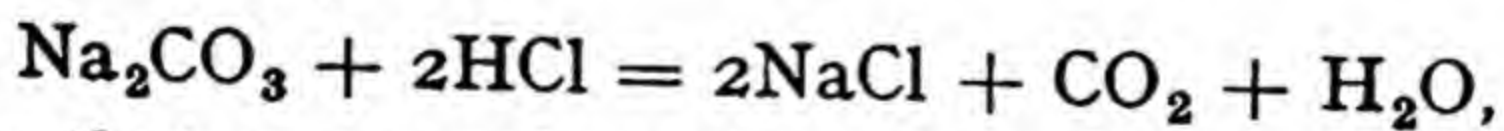
it follows that a normal solution of sodium carbonate is also a semi-molar solution, and will therefore contain 53.0 grams of Na_2CO_3 per litre.

Decinormal and Centinormal Solutions

In many volumetric estimations it is more convenient, and more accurate, to work with solutions weaker than normal,

* Equivalent to.

and, for such purposes, decinormal and centinormal solutions are frequently employed. A *decinormal* solution is, as its name denotes, a 0·1 normal solution, and, therefore, contains one-tenth of the gram-equivalent of the reagent per litre ; a centinormal solution is a 0·01 normal solution, and contains one-hundredth of the gram-equivalent of the reagent per litre. In general, decinormal solutions are very widely used, though, in all cases, that standard solution which gives the sharpest 'end-point' with the indicator should be employed.

5. THE VARIATION OF NORMALITY. We have seen that normality is dependent on the equivalent of a substance, and that it is related to the molecular weight of the substance ; but, whereas the molecular weight of a compound is a fixed magnitude, the equivalent, and consequently the normality, depends entirely on the reaction in which that compound takes part. This is analogous to those cases in which elements exhibit more than one valency ; for example, the atomic weight of phosphorus is an invariable quantity, namely, 31 ; but, in the compounds PH_3 and P_2H_4, the equivalent of phosphorus is 10·33 and 15·5 respectively. Thus the chemical equivalent of phosphorus is variable, and its magnitude depends upon the reaction in which the phosphorus takes part.

The same principle applies to the chemical equivalents of compounds. For example :

(1) (a) *Sodium hydrogen sulphate* reacts with sodium hydroxide according to the equation :

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O.$$
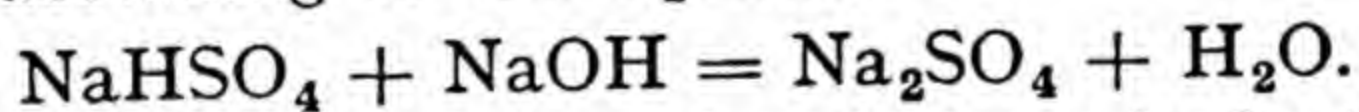
For this reaction, then, the chemical equivalent of sodium hydrogen sulphate will be identical with the molecular weight, and a normal solution of sodium hydrogen sulphate will be a molar solution.

(b) Sodium hydrogen sulphate, however, reacts with barium chloride in the following way :

$$NaHSO_4 + BaCl_2 = NaCl + HCl + BaSO_4.$$
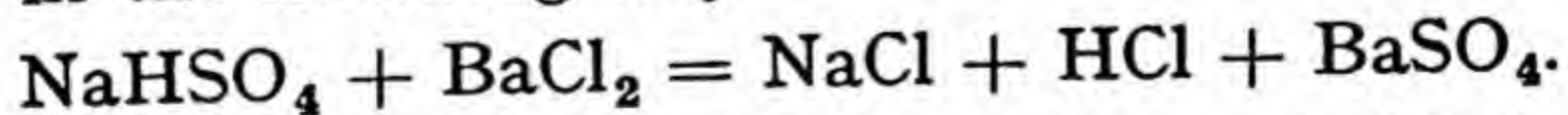
In this case, since 1 molecule of barium chloride is equivalent to 2 molecules of NaOH, it follows that the chemical equivalent of sodium hydrogen sulphate is equal to half the molecular weight. For this reaction, therefore, a normal solution of sodium hydrogen sulphate will be a semi-molar solution.

(2) The chemical equivalent of *potassium permanganate*

depends upon the way in which it is employed as an oxidizing agent.

(a) In acid solution, *two* molecules of potassium permanganate liberate *five* atoms of ' available ' oxygen.

Therefore, $2KMnO_4 \equiv 5O \equiv 10H,$

i.e. $KMnO_4 \equiv 5H.$

Thus, when potassium permanganate is to be employed as an oxidizing agent in acid solution, a normal solution will contain one-fifth of the gram-molecular weight per litre.

(b) When, however, potassium permanganate is used as an oxidizing agent in alkaline or neutral solution, *two* molecules of the permanganate liberate *three* atoms of ' available ' oxygen.

Therefore, $2KMnO_4 \equiv 3O \equiv 6H,$

i.e. $KMnO_4 \equiv 3H.$

Thus, when potassium permanganate is to be employed in alkaline (or neutral) solution, a normal solution will be equivalent to a one-third molar solution.

(3) (a) *Potassium bi-iodate* reacts as an acid with alkalies, viz. :

$$KH(IO_3)_2 + KOH = 2KIO_3 + H_2O.$$
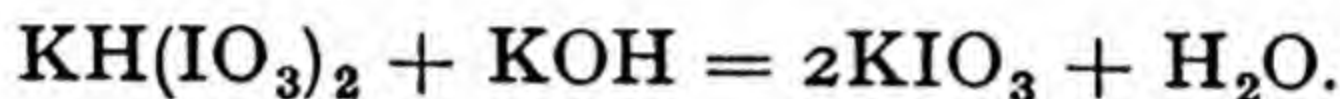
Thus, since *one* molecule of the bi-iodate is equivalent to *one* molecule of KOH, it follows that where potassium bi-iodate is to be employed as an acid a normal solution will be the same as a molar solution.

(b) Potassium bi-iodate also reacts as an oxidizing agent, liberating iodine from potassium iodide solution in the presence of dilute acid :

$$KH(IO_3)_2 + 10KI + 11HCl = 6I_2 + 11KCl + 6H_2O.$$
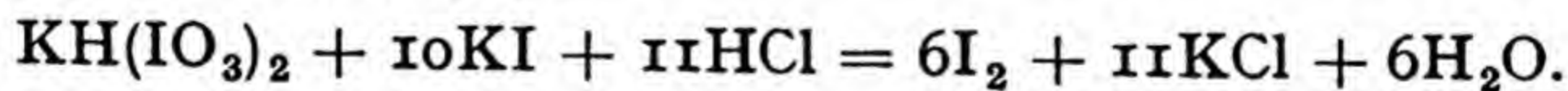
Here, $KH(IO_3)_2 \equiv 12I \equiv 12H.$

Therefore, in this particular reaction, a normal solution of potassium bi-iodate would be a *one-twelfth molar* solution.

It will be seen readily from the three typical cases studied above that normality is not fixed, but that it can vary, and that its value depends entirely upon the particular reaction in which the particular reagent is to be used.

6. CALCULATION OF RESULTS WHEN USING NORMAL SOLUTIONS. Suppose that a volume n_1 c.c. of a solution A require n_2 c.c. of a normal solution B to effect the colour

change with a certain indicator, then, the normality of the solution A, with respect to B, will be

$$N \times \frac{n_2}{n_1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(i)$$

If the solution B were decinormal, then the normality of the solution A would be

$$0 \cdot 1N \times \frac{n_2}{n_1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(ii)$$

The strength of the solution A, in grams per litre, would then be found by substituting the chemical equivalent of A in the particular reaction, for N in either (i) or (ii) according whether the solution B were normal or decinormal.

For example, suppose that 20·0 c.c. of NaOH solution required, as a mean of three titrations, 25·0 c.c. of decinormal sulphuric acid for complete neutralization, then the normality of the NaOH solution is

$$0 \cdot 1N \times \frac{25}{20},$$

and, since the chemical equivalent of NaOH is 40·0, the strength of the alkaline solution is $4 \cdot 0 \times \frac{25}{20}$, or 5·0 grams, NaOH per litre.

7. ERRORS IN VOLUMETRIC ANALYSIS. It was stated in § 2 that the accuracy of a volumetric determination depends upon the purity of the reagent employed, the sensitiveness of the indicator, and the accuracy of the measuring vessels used in the determination. There are, however, several precautions which should be observed in any volumetric estimation. The measuring vessels—burettes, pipettes, graduated flasks, etc.—should be thoroughly cleaned, and washed out with a little of the solution they are to contain. Moreover, in taking the reading of a burette where a rapid titration has been necessary, the solution must be allowed to drain down the sides of the burette before the volume of liquid is measured ; this is necessary since the volume of liquid left on the walls of the vessel after a rapid titration may easily amount to 0·2 c.c., and, if a fairly strong solution is being used, the error introduced would be comparatively high. For the same reason, when using a pipette, the liquid must be allowed to run out slowly, so that the minimum amount of solution adheres to the sides ; the last drop of

liquid remaining in the pipette must be expelled, and this is best done by placing a finger over the top of the pipette and gently squeezing the glass bulb: the drop of liquid is then expelled by the expansion of the air in the pipette.

As a general rule it is preferable to work with decinormal solutions, since a slight error in reading the burette will not give so large an error in the result as when a normal solution had been used. It must be remembered, however, that the accuracy of an estimation also depends upon the sensitiveness of the indicator, and, in one or two cases, the ' end-point ' of the reaction is more definite with strong solutions.

It must also be borne in mind that the accuracy of ordinary pipettes, burettes, etc., is generally of the order $\pm$ 0·5 per cent, and, if greater accuracy than this is required, it is necessary to calibrate the measuring vessels by filling them to their capacity with water and weighing the contents. This should be done at the temperature at which the instrument was originally graduated. In the case of a burette greater accuracy could be obtained by calibrating each cubic centimetre and then plotting the errors in the form of a graph which can be referred to in every case where that particular burette is used. The actual weighing should be carried out only a little way beyond the degree of accuracy required in the burette. For example, in calibrating a burette graduated in tenths of cubic centimetres, it is pointless to weigh more accurately than to one milligram.

A typical curve for the calibration of a burette is shown in Fig. 1.
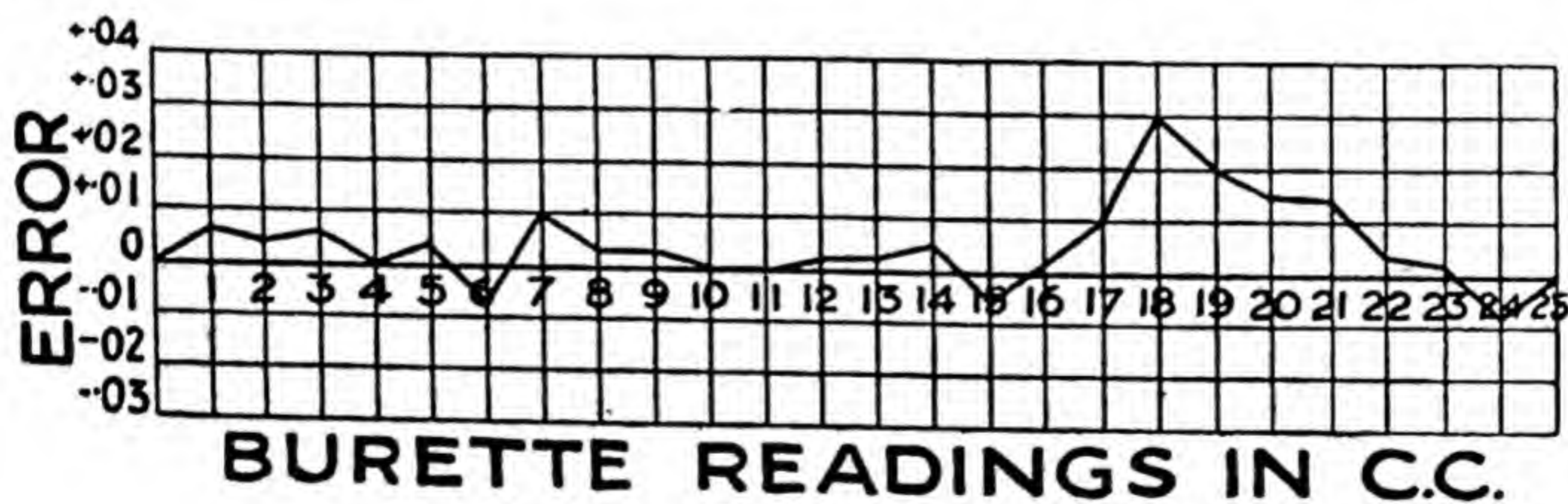
FIG. 1

CALIBRATION CURVE FOR A BURETTE

Care must also be taken in reading the volume of liquid in a burette to avoid error by parallax. The meniscus in aqueous solutions is curved downwards, and thus appears to have an upper and a lower margin: the reading must

always be taken at the middle point of the lower margin, and, in taking the reading, the eye should always be on a level with the lower margin of the meniscus. In Fig. 2 it will
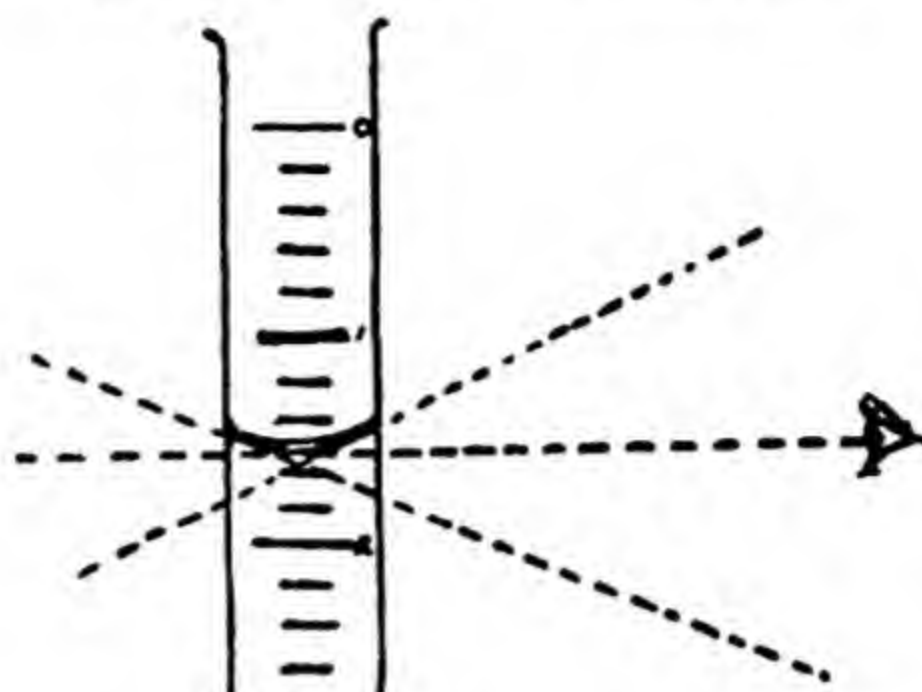
FIG. 2

PARALLAX ERROR

be observed how incorrect readings are obtained if this precaution be neglected.

In all cases where heat has been employed in order to prepare a standard solution, the solution must be allowed to cool to the temperature of the room before any determination is made with the solution. This precaution is very necessary since the thermal expansion of liquids is of comparatively large magnitude.

8. CONCORDANT RESULTS. In any titration a rough estimation should be made first of all in order to obtain an approximate idea of the volume of solution required. The titration should then be determined accurately, and this result repeated twice more, at least—the average value of these titrations being taken as the volume of solution required to complete the chemical reaction. These results should not differ by more than 0·2 c.c. at the very most—in fact, a difference of 0·1 c.c. is all that should be permitted—and, if any titration be at all doubtful, the experiment must be repeated until, at least, three concordant results have been obtained. In this way the margin of experimental error is considerably minimized, and it cannot be too strongly stressed that several concordant readings must be obtained in any volumetric estimation.

In most cases of titration it is immaterial whether the standard solution or the solution of unknown strength be placed in the burette. It is generally more convenient for the calculations if the standard solution be run into a convenient volume of the solution which has to be determined.

There are, however, one or two reactions in which the colour change of the indicator is more sharply defined if the titration is carried out in one particular direction ; for example, in titrating an iodine solution with standard sodium thio-sulphate solution it is better to run the thiosulphate solution into the iodine solution, and to add the indicator (starch solution) just before the colour of the iodine disappears. Again, when solutions of NaOH, KOH, and particularly $Ba(OH)_2$ are employed, these solutions should be placed in the burette, as they are liable to be affected by the atmospheric carbon dioxide ; by this precaution the surface area of the liquid exposed to the air is reduced to a minimum. Except for these special cases, however, it is unimportant which way the titration proceeds.

9. INDICATORS. (a) *Neutrality and Equivalence.* It is important, at the outset, to recognize clearly the difference between *Neutrality* and *Equivalence.* It is found, for example, *in titrating sodium carbonate with standard HCl* that, using *phenolphthalein* as the indicator, the colour change occurs when the carbonate has been converted to the bicarbonate. *An equivalent amount of acid has been added to the alkaline carbonate, but the carbonate has been only half-neutralized*, viz. :

$$Na_2CO_3 + HCl = NaCl + NaHCO_3.$$
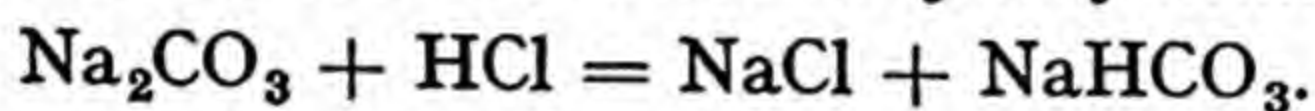
If, however, in the same titration, *methyl orange* is employed as the indicator, the colour change occurs when the decomposition of the carbonate is completed, viz. :

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$
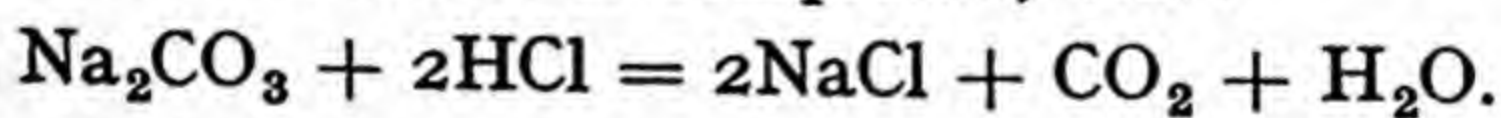
Here, equivalence and neutrality coincide.

Again, when *titrating orthophosphoric acid with NaOH* using *methyl orange* as indicator, the colour change occurs when one of the three replaceable hydrogen atoms in the acid molecule has been replaced by sodium, viz. :

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$
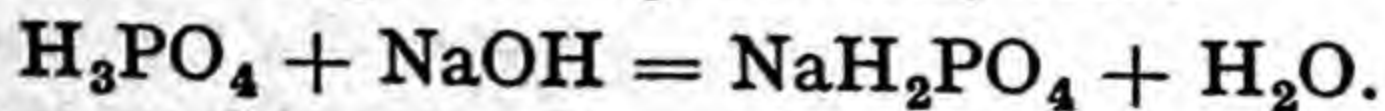
Equivalence and neutrality are not identical here.

In the same titration, if *phenolphthalein* is the indicator, the colour change occurs when two hydrogen atoms in the acid molecule have been replaced, viz. :

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O.$$
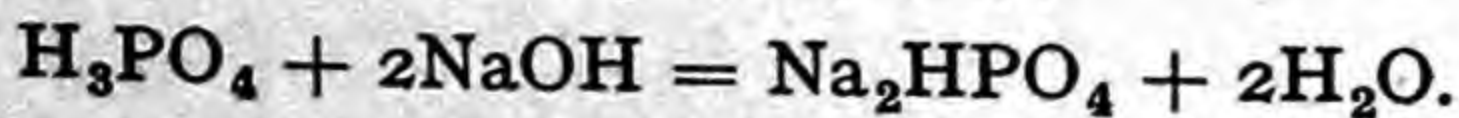
Here, again, neutrality and equivalence are not identical. In fact, no satisfactory indicator has yet been found which will

denote the true neutralization point of orthophosphoric acid by a strong base.

(b) *Can any indicator be used in titrating any acid and base?* We have just seen that the true function of an indicator is to show when an *equivalent* amount of acid or base has been added in a *particular* titration. The question at once arises : ' Can any indicator be used in titrating any acid or base ? ' This can be answered experimentally in the following simple way. If we prepare solutions of various salts, the same concentration being obtained in each case, we have *a series of solutions containing equivalent amounts of acid and base.* We can then watch the effect of various indicators on the solutions.

	Litmus	Phenol-phthalein	Paranitro-phenol	Methyl Orange
N.NaCl	Neutral	*Neutral ?	Neutral	Neutral
N.KCN	Alkaline	Alkaline	Alkaline	Alkaline
N.NH$_4$Cl	Slightly acid	*Acid (?)	Neutral (approx.)	Neutral (approx.)
N.AlCl$_3$	Acid	*Acid (?)	Acid	Neutral (approx.)

Experiment. Prepare decinormal solutions (100 c.c.) of the following salts :

(a) *NaCl* (the salt of a strong base, NaOH, and a strong acid, HCl. We have, therefore, in solution, equivalent quantities of NaOH and HCl) ;

(b) *KCN* (the salt of a strong base, KOH, and a weak acid, HCN. We thus obtain a solution containing equivalents of KOH and HCN) ;

(c) *NH$_4$Cl* (the salt of a weak base, NH$_4$OH, and a strong

* Since phenolphthalein is colourless in neutral and acid solution, it is impossible to say, from this experiment alone, whether the solutions are acidic or neutral.

acid, HCl. The solution contains, therefore, equivalent amounts of NH₄OH and HCl) ;

(d) *AlCl₃* (the salt of a very weak base, Al(OH)₃, and a strong acid, HCl. We have, therefore, a solution containing equivalents amounts of Al(OH)₃ and HCl).

To 25 c.c. of each solution add one drop of *litmus* ; to a further 25 c.c. of each solution add one drop of *phenolphthalein* ; then add one drop of *paranitrophenol* to 25 c.c. of each solution, and to the last 25 c.c. of each solution add one drop of *methyl orange.*

In such an experiment the results shown in the Table on the opposite page were obtained.

It will be noticed that, except in the case of NaCl, the various indicators employed do not indicate equivalence in every case although the solutions contain equivalent amounts of acid and base. We come to the conclusion, therefore, that any indicator will not give identical results in all titrations. The reasons for this are to be discovered in a study of the Hydrolysis of Salt solutions.

THE HYDROLYSIS OF SALT SOLUTIONS

(a) *The salt of a strong acid and a strong base.* We will consider the case of sodium chloride, the salt of a strong acid, HCl, and a strong base, NaOH. The salt is, therefore, highly dissociated in dilute solution into electropositive and electronegative ions, viz. :

$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl} ;$$
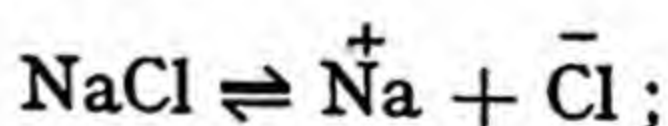
but the solvent water is dissociated feebly into electropositive hydrogen ions and electronegative hydroxyl ions :

$$H_2O \leftrightharpoons \overset{+}{H} + \overset{-}{OH}.$$
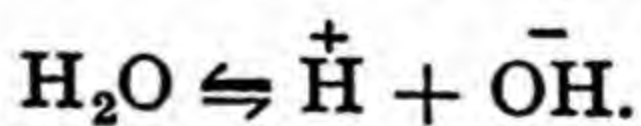
The hydrogen ions from the water will combine with the chlorine ions to form HCl, but this, being a strong acid, is practically fully dissociated, so that the hydrogen ion concentration remains unaltered.

Similarly, the NaOH, a strong base, formed by the union of the sodium ions and the hydroxyl ions from the water, is fully dissociated, and the concentration of the hydroxyl ions remains unaltered.

Thus, since the concentrations of hydrogen and hydroxyl ions are equal, and since acidity is due to hydrogen ions, and alkalinity to hydroxyl ions, the NaCl solution will be neutral.

(b) *The salt of a strong base and a weak acid.* A solution of potassium cyanide, as we have seen in the preceding experiment, is not neutral towards the common indicators. The KCN, just like the NaCl, is highly dissociated into electropositive and electronegative ions, and the water is slightly dissociated into hydrogen and hydroxyl ions. The $\overset{+}{H}$ ions unite with the $\overset{-}{CN}$ ions to form HCN, which, being a weak acid, is only feebly dissociated :

$$KCN \rightleftharpoons \overset{+}{K} + \overset{-}{CN}$$
$$H_2O \rightleftharpoons \overset{-}{OH} + \overset{+}{H}$$
$$\Updownarrow$$
$$HCN$$
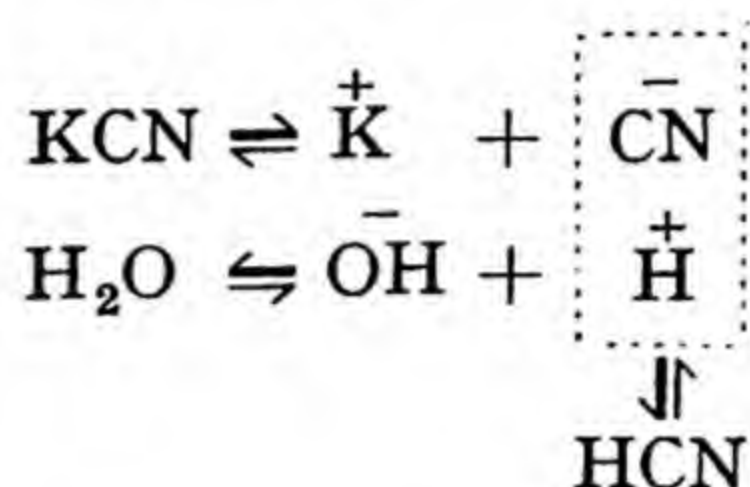
Thus, as the $\overset{+}{H}$ and $\overset{-}{CN}$ ions unite to form feebly dissociated HCN, more water molecules must dissociate to replace the $\overset{+}{H}$ ions removed from the solution and restore the equilibrium $H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{OH}$.

Thus, when equilibrium is again attained, there is an excess of $\overset{-}{OH}$ ions in the solution, and, consequently, the solution will give an alkaline reaction with suitable indicators.

In the same way, alkaline carbonates undergo hydrolytic dissociation, and owing to the excess of $\overset{-}{OH}$ ions in the solution, at equilibrium, give an alkaline reaction with most indicators, viz. :

$$Na_2CO_3 \rightleftharpoons \overset{+}{Na} + \overset{+}{Na} + \overset{=}{CO_3}$$
$$2H_2O \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{+}{H} + \overset{+}{H}$$
$$\Updownarrow$$
$$H_2CO_3$$
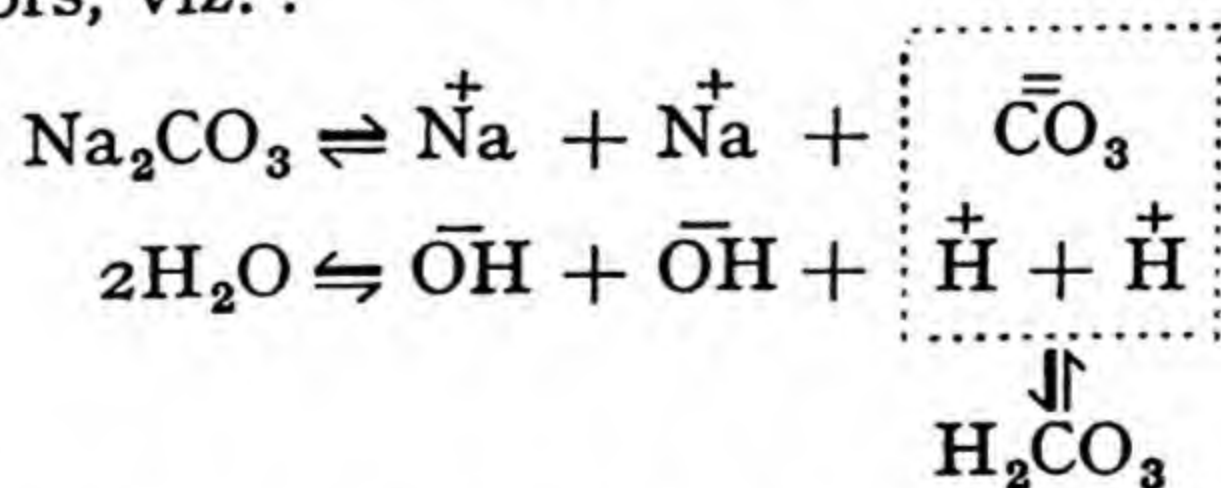
(c) *The salt of a weak base and a strong acid.* In a manner analogous to that for the case of KCN, an aqueous solution of ammonium chloride, the salt of a weak base, NH_4OH, and a strong acid, HCl, will give an acid reaction owing to the excess of $\overset{+}{H}$ ions in the solution. The $\overset{+}{NH_4}$ ions unite with

the $\overline{OH}$ ions from the water to form NH_4OH, which, being a weak base, is only feebly dissociated :

$$NH_4Cl \rightleftharpoons \overset{+}{NH_4} + \overset{-}{Cl}$$

$$H_2O \rightleftharpoons \overset{-}{OH} + \overset{+}{H}$$

$$\Updownarrow$$

$$NH_4OH$$
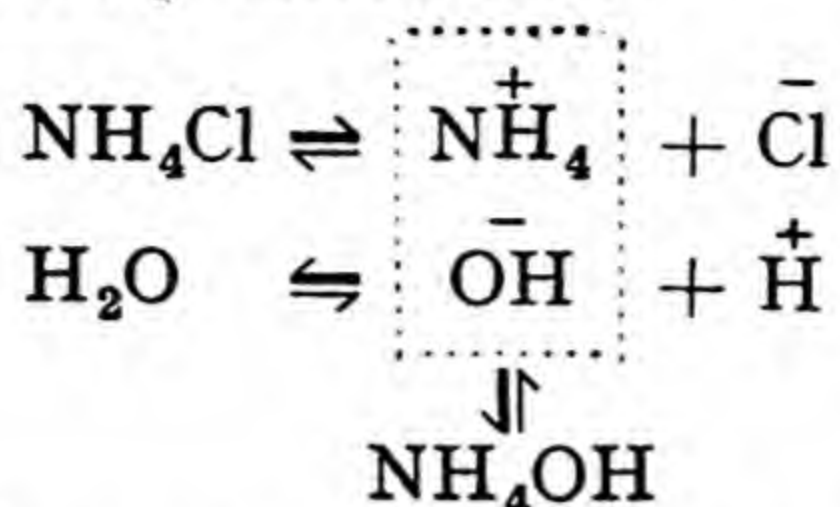
Thus, as the $\overline{OH}$ ions are removed from the equilibrium by combination with the $\overset{+}{NH_4}$ ions, more water molecules will dissociate in order to restore the equilibrium $H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{OH}$. Thus, when equilibrium is again attained, there is an excess of $\overset{+}{H}$ ions in the solution which will give an acid reaction with suitable indicators.

It will thus be seen that a study of the hydrolysis of salt solutions is of fundamental importance in the theory of indicators. This subject is treated more fully in Chapter X, but it will be obvious that one particular indicator may be suitable only for one, or more, special reactions. Brief accounts of the indicators in common use will be found in § 142 and should be studied in conjunction with the rest of Chapter X.

External Indicators. In many volumetric estimations it has been found convenient to employ an indicator apart from the reacting solutions. In the actual determination, a drop of the reacting solutions is removed on the end of a glass rod, at frequent intervals, and mixed with the indicator, which is generally placed in small, separate drops on a white tile. For example, potassium ferricyanide is employed as an external indicator in the estimation of iron in a ferrous salt, by means of standard potassium dichromate solution (see § 50). These external indicators are generally employed in determinations other than those involving acidimetric or alkalimetric methods, and, in consequence, the 'end-point' is based almost entirely on a colour change which may, in some cases, be independent of the degree of ionization of the solution. It is difficult, therefore, to formulate any general rules for the behaviour of external indicators, and each particular case will be dealt with in the particular determination in which it is employed.

2

CHAPTER II

ACIDIMETRY AND ALKALIMETRY

10. The first care in estimating solutions of acids and bases is to ensure that the standard solution used is pure and accurately prepared. The strengths of solution generally employed are Normal or Decinormal, and the common reagents in acidimetry and alkalimetry are as follows :

Acids.—Hydrochloric, sulphuric, nitric ; and, less frequently, oxalic and acetic.

Bases.—Sodium hydroxide, potassium hydroxide, sodium carbonate (which is alkaline in solution owing to hydrolytic dissociation), and, occasionally, baryta water (barium hydroxide solution).

In preparing standard solutions of these reagents it is usual to choose one of them as the basis for the preparation of the others ; the one frequently selected is sodium carbonate, since a standard solution of this compound can be prepared with a high degree of accuracy. When the standard carbonate solution has been made, a solution of sulphuric acid is then standardized with respect to the sodium carbonate ; from the acid thus prepared a solution of sodium hydroxide may be standardized, and so on until standard solutions of all the required reagents have been obtained.

11. NORMAL SODIUM CARBONATE. Sodium carbonate is alkaline in solution on account of hydrolysis and reacts with acids liberating carbon dioxide and water. (For the explanation of the hydrolytic dissociation, see § 9).

In the case of hydrochloric acid, the reaction is :

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O ;$$

or, according to the ionic hypothesis :

$$Na_2CO_3 \rightleftharpoons \overset{+}{Na} + \overset{+}{Na} + \overline{\overline{C}O_3}$$

$$2HCl \rightleftharpoons \overline{Cl} + \overline{Cl} + \overset{+}{H} + \overset{+}{H}$$

$$\Updownarrow$$

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O.$$
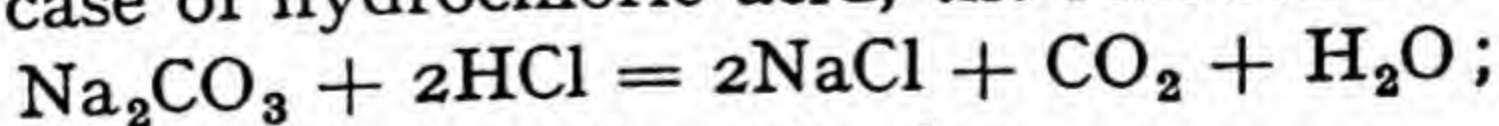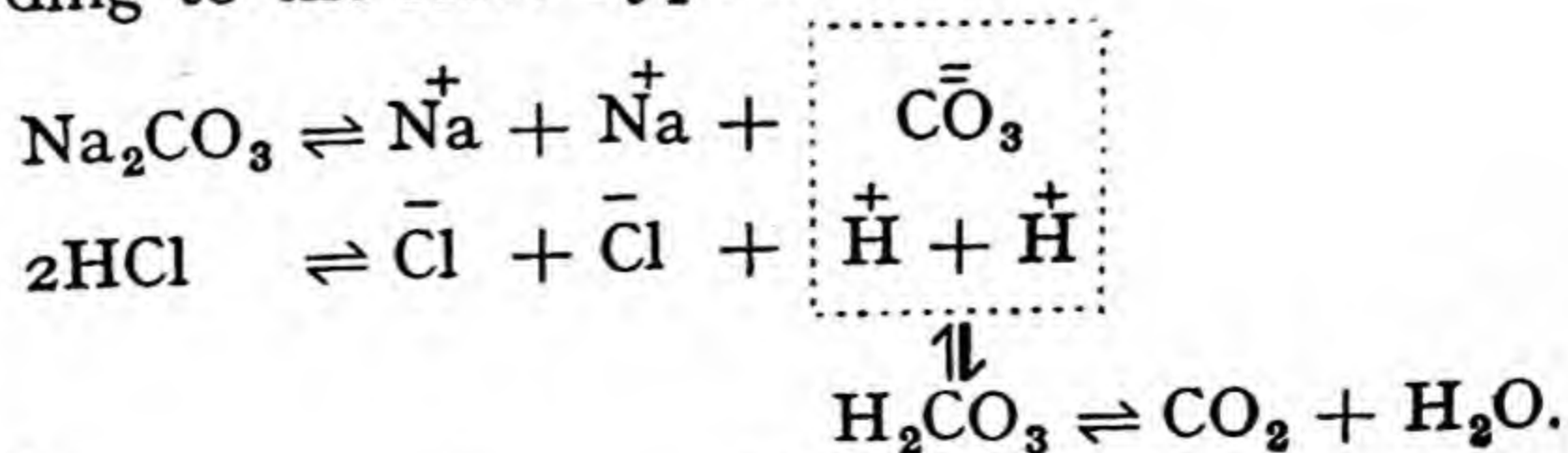
Here, $Na_2CO_3 \equiv 2HCl \equiv 2H.$

Therefore, 106 grams of $Na_2CO_3 \equiv 2$ grams of H; i.e. the chemical equivalent of Na_2CO_3 is $\dfrac{106}{2}$, or 53.

Thus, a normal solution of sodium carbonate will be a semi-molar solution and will contain 53 grams of the pure, anhydrous salt per litre.

The salt is best obtained in a state of purity by heating pure, recrystallized sodium bicarbonate (as this substance has only a slight solubility in water it can be easily purified by recrystallization). The salt must not be allowed to fuse, but should be heated at dull red heat for about twenty minutes; it should be cooled in the desiccator, weighed, and then heated for short intervals, and the cooling and weighing repeated until a constant weight is obtained; this ensures the complete decomposition of the bicarbonate according to the equation :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
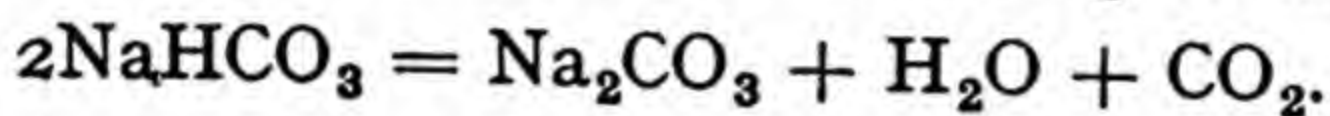
In preparing a normal solution of Na_2CO_3 it is found convenient to take about 85 grams of sodium bicarbonate; this should yield on heating about 54·5 grams of the normal carbonate. This anhydrous carbonate is then weighed accurately, dissolved in distilled water, and made up to the required volume for accurate normal strength.

For example, suppose that 54·325 grams of the carbonate were dissolved in about 500 c.c. of distilled water, the correct volume would be calculated as follows :

53·0 grams of Na_2CO_3 are contained in 1000 c.c. of normal solution ;

$\therefore$ 54·325 grams of Na_2CO_3 are contained in $\dfrac{1000 \times 54·325}{53}$, or 1025 c.c. of normal solution.

The 500 c.c. of solution would be made up to 1025 c.c. with distilled water, and would, then, be accurately normal. A solution of 0·1N·Na_2CO_3 could be easily obtained by measuring out 100 c.c. of the normal solution, and diluting to 1 litre with distilled water.

12. NORMAL SULPHURIC ACID. Ordinary strong sulphuric acid contains about 92% of pure H_2SO_4, and reacts with sodium carbonate according to the equation :

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O ;$$
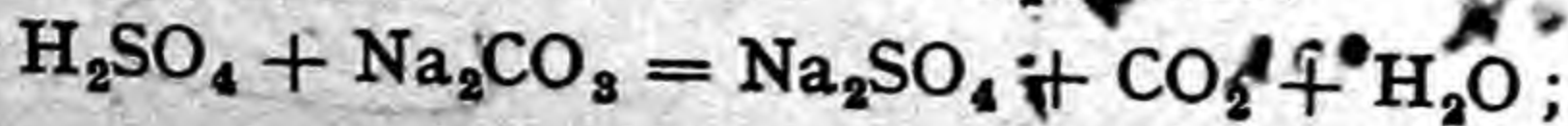
or, depicting the reactions to be between the respective ions :

$$H_2SO_4 \rightleftharpoons \overset{+}{H} + \overset{-}{HSO_4}$$

$$\overset{+}{H} + \overset{=}{SO_4}$$

$$Na_2CO_3 \rightleftharpoons \overset{=}{CO_3} + \overset{+}{Na} + \overset{+}{Na}$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2.$$
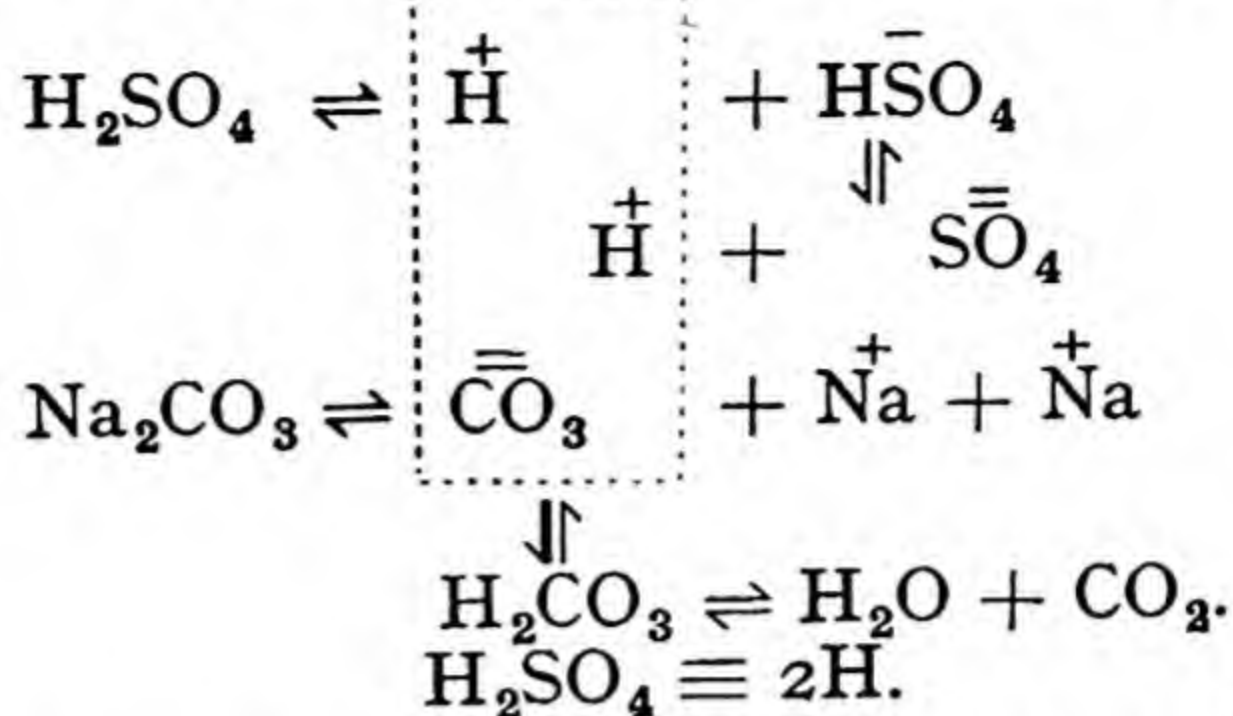
Here,
$$H_2SO_4 \equiv 2H.$$

Therefore, the chemical equivalent of H_2SO_4 is $\dfrac{98}{2}$, or 49.

Thus, a normal solution of sulphuric acid will be a semi-molar solution, and will contain 49 grams of pure H_2SO_4 per litre.

The specific gravity of ordinary concentrated sulphuric acid is 1·84, so 49 grams of the strong acid will have a volume of about 27 c.c.

To prepare a normal solution of H_2SO_4, 30 c.c. of the strong acid are carefully added to a sufficient excess of distilled water, the solution is allowed to cool to the temperature of the room, and then made up to one litre. This solution is, thus, slightly stronger than normal, and it is then titrated with the normal sodium carbonate solution, using one drop of methyl orange as indicator. Three concordant results are obtained and the amount of water required to be added to the acid solution to make it accurately normal is then calculated.

For example, suppose that, as a mean of three titrations, 23 c.c. of the sulphuric acid solution were required to neutralize exactly 25 c.c. of the $N.Na_2CO_3$ solution. Then, since a given volume of a normal base is equivalent to exactly the same volume of a normal acid, it follows that 2 c.c. of water must be added to every 23 c.c. of the sulphuric acid solution to make it accurately normal; or, expressing this result in a more convenient form, 1 litre of the acid solution will require the addition of 87 c.c. of distilled water to bring it to accurately normal strength.

A decinormal solution of H_2SO_4 can then be prepared by taking 100 c.c. of the normal solution and diluting it to 1 litre with distilled water.

13. NORMAL SODIUM HYDROXIDE, AND NORMAL POTASSIUM HYDROXIDE. Sodium hydroxide reacts with sulphuric acid according to the equation :

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O ;$$
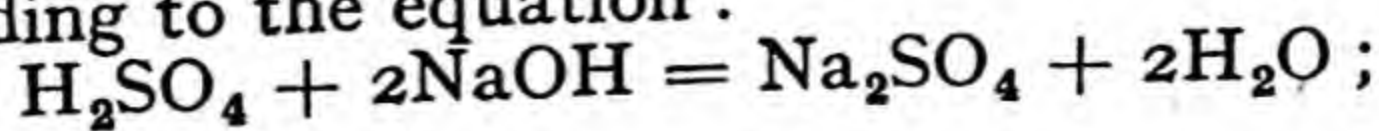
or, depicted in terms of ions :

$$H_2SO_4 \rightleftharpoons \overset{+}{H} + \overset{-}{H}SO_4$$
$$\overset{+}{H} + \overset{=}{S}O_4$$
$$2NaOH \rightleftharpoons \overset{-}{O}H + \overset{-}{O}H + \overset{+}{N}a + \overset{+}{N}a$$
$$2H_2O$$

Here, $2NaOH = H_2SO_4 \equiv 2H$;

i.e. $NaOH \equiv H.$
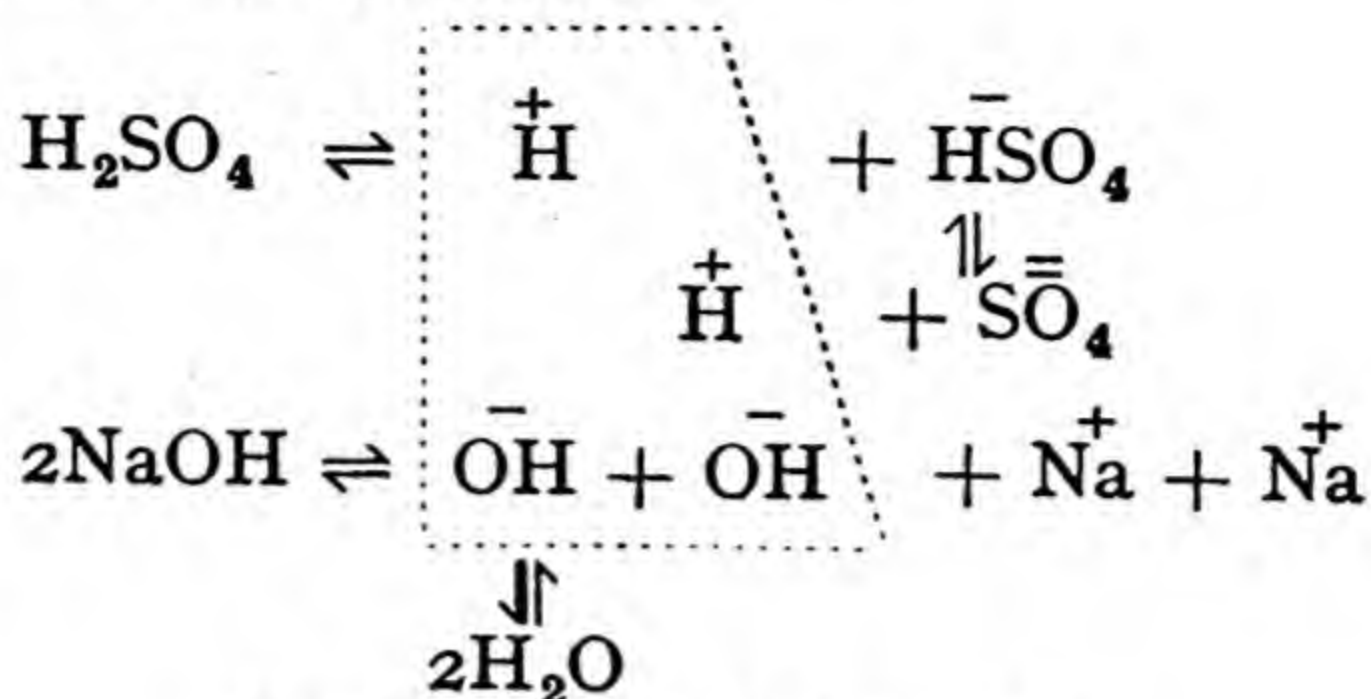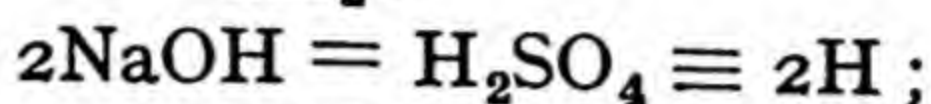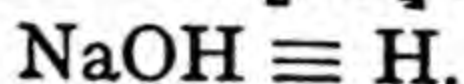
Thus, the chemical equivalent of NaOH is the same value as the molecular weight, i.e. 40, and, consequently, a normal solution of the alkali will be a molar solution and will contain 40 grams of pure NaOH per litre.

As the purest commercial caustic soda seldom contains more than 98% NaOH, it is best to take about 43 grams of the pure, stick sodium hydroxide, dissolve it in distilled water, and then make up the solution to 1 litre. This can then be titrated with the normal sulphuric acid using litmus as indicator, and the volume of water which must be added to make the solution accurately normal can then be calculated in the same way as before ; e.g. :

If, say, as a mean of three titrations, 25·0 c.c. of the N.H$_2$SO$_4$ require 23·5 c.c. of the NaOH solution for complete neutralization, then 1·5 c.c. of distilled water must be added to every 23·5 c.c. of the alkaline solution to make it accurately normal ; i.e. 64 c.c. must be added to 1 litre of the NaOH solution.

In the same manner 2 molecules of potassium hydroxide react with 1 molecule of sulphuric acid according to the equation :

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O ;$$

or,

$$H_2SO_4 \rightleftharpoons \overset{+}{H} + \overset{-}{H}SO_4$$
$$\overset{+}{H} + \overset{=}{S}O_4$$
$$2KOH \rightleftharpoons \overset{-}{O}H + \overset{-}{O}H + \overset{+}{K} + \overset{+}{K}$$
$$2H_2O$$

Here, $$2KOH \equiv H_2SO_4 \equiv 2H;$$

i.e. $$KOH \equiv H.$$
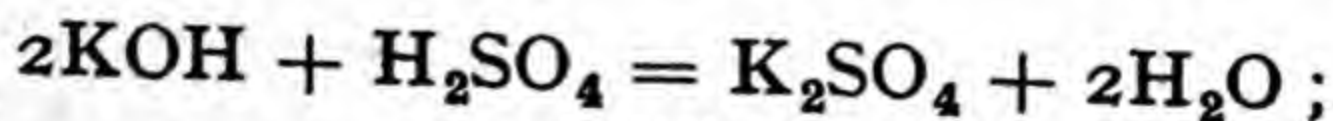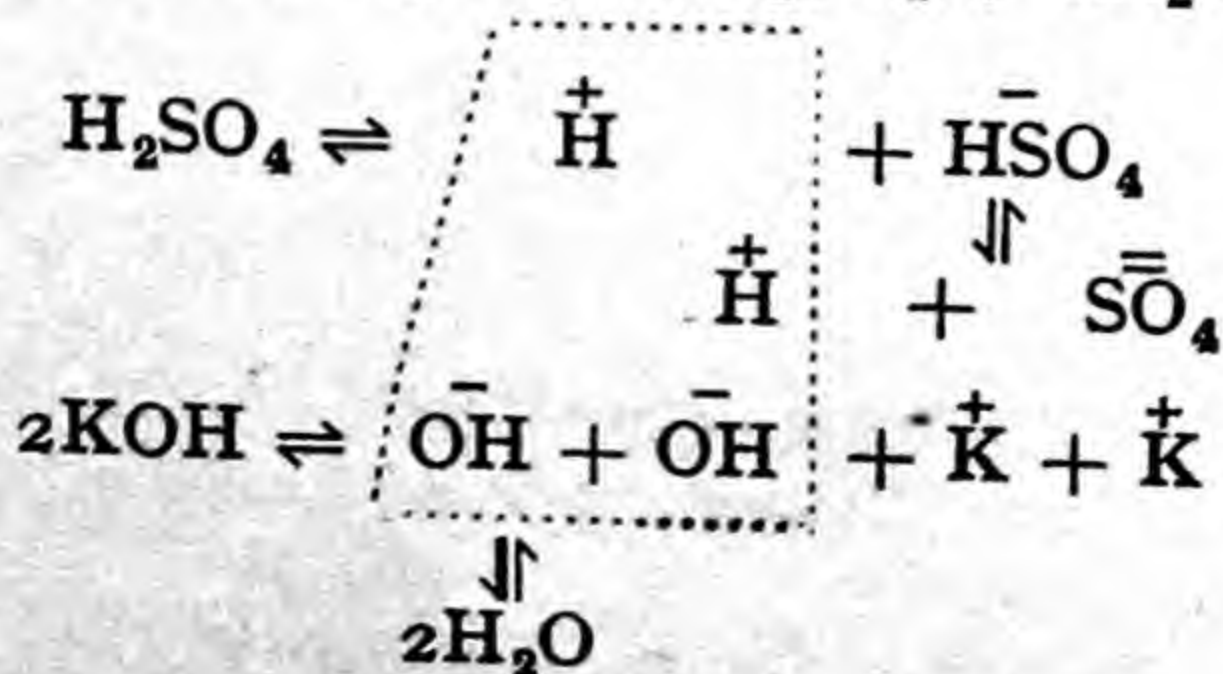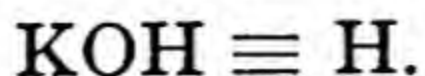
Thus, the chemical equivalent of KOH is also the same value as the molecular weight, and a normal solution of the alkali will be a molar solution, and will contain 56 grams of pure KOH per litre.

In preparing the normal solution the same method will be employed : a solution of KOH slightly stronger than normal (say 60 grams of the pure, stick KOH dissolved in 1 litre of water) will be made up, titrated with $N.H_2SO_4$, using litmus as indicator, and the volume of water which must be added to 1 litre of the alkaline solution to make it accurately normal calculated as before.

14. NORMAL NITRIC ACID. Nitric acid reacts with sodium hydroxide according to the equation :

$$HNO_3 + NaOH = NaNO_3 + H_2O;$$

or,

$$HNO_3 \rightleftharpoons \overset{+}{H} + \overset{-}{NO_3}$$

$$NaOH \rightleftharpoons \overset{-}{OH} + \overset{+}{Na}$$

$$\Updownarrow$$

$$H_2O$$

Here, $$HNO_3 \equiv NaOH \equiv H.$$
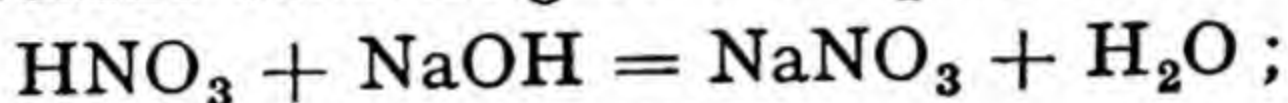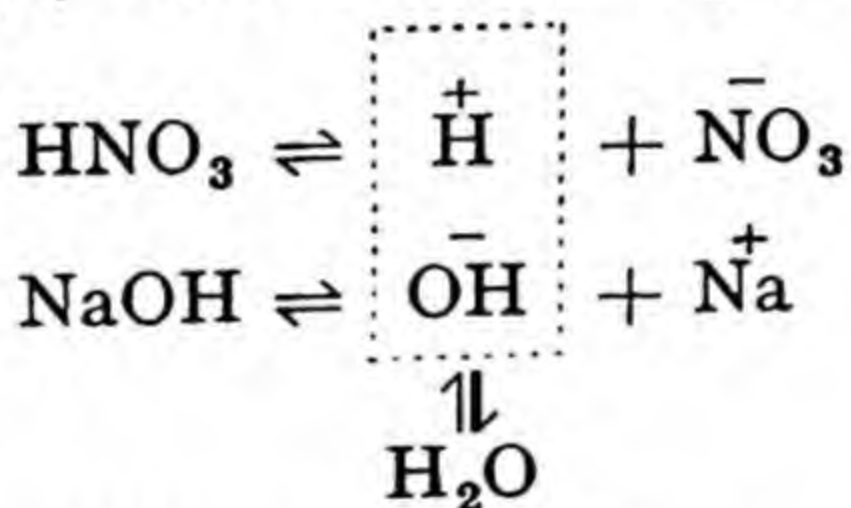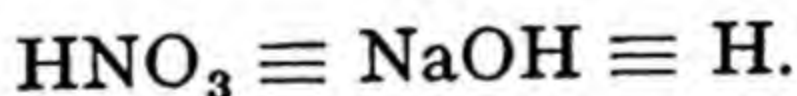
Therefore the chemical equivalent of HNO_3 is the same as the molecular weight, and a normal solution of the acid will be a molar solution containing 63 grams of pure HNO_3 per litre.

In preparing the normal solution, the same procedure is observed : a solution of nitric acid slightly stronger than normal is prepared (as ordinary strong nitric acid of specific gravity 1·42 contains about 70% pure HNO_3, it is advisable to make up about 95 grams (67 c.c., S.G. 1·42) of the ordinary strong nitric acid to 1 litre). Aliquot portions of this solution are then titrated with normal NaOH, using litmus as indicator, and the acid is then standardized as in the preceding cases.

15. NORMAL HYDROCHLORIC ACID. It is obvious that, since hydrochloric acid reacts with sodium hydroxide according to the equation :

$$NaOH + HCl = NaCl + H_2O;$$

or, expressing the reaction in terms of ions :

$$NaOH \rightleftharpoons \overset{+}{Na} + \boxed{\overset{-}{OH}}$$

$$HCl \rightleftharpoons \overset{-}{Cl} + \boxed{\overset{+}{H}}$$

$$\Updownarrow$$

$$H_2O$$
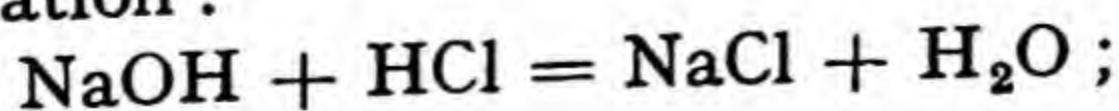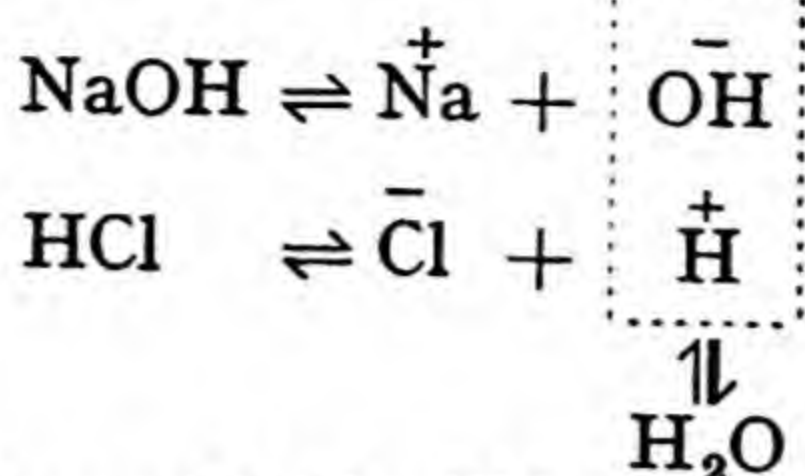
that a normal solution of HCl will be a molar solution, and will contain 36·5 grams of pure HCl per litre. A solution of HCl slightly stronger than normal could be prepared, titrated with normal NaOH, and diluted to the calculated volume in order to make it accurately normal. (As ordinary strong HCl solution of specific gravity 1·16 seldom contains more than 30% HCl, it is best to make up about 125 grams— 108 c.c.—of strong acid to 1 litre for the preliminary solution.)

16. OTHER METHODS OF STANDARDIZING HYDROCHLORIC ACID. It was stated in § 10 that, in preparing standard solutions of acids and bases, it is usual to choose one that can be made up with a great degree of accuracy and then standardize other reagents with respect to that solution. This is the method we have followed, using sodium carbonate as the standard, and it is generally the best method. It is also customary, however, to prepare a standard solution of HCl and use that as the basis for making the other standard solutions. There are several ways in which this can be done, and details of these methods are given below.

(a) *Standardization of HCl by means of Iceland Spar.* Iceland Spar is the purest, crystalline form of calcium carbonate, and it will react with hydrochloric acid according to the equation :

$$\underset{100}{CaCO_3} + \underset{2 \times 36·5}{2HCl} = CaCl_2 + CO_2 + H_2O$$
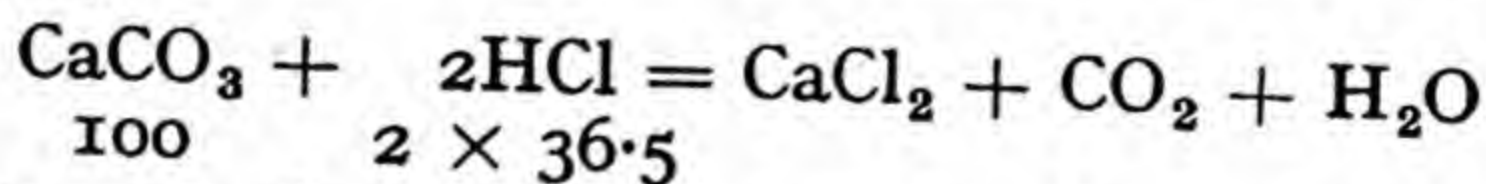
It will be seen that, since the molecular weight of $CaCO_3$ is 100, 100 grams of pure $CaCO_3$ will require exactly 2 litres of N.HCl for complete decomposition. Therefore, 1 gram of Iceland Spar is exactly equivalent to 20 c.c. of N.HCl.

Method. About 2 or 3 grams of Iceland Spar broken into small fragments are placed in a clean, dry beaker and carefully weighed. A measured volume of the hydrochloric acid it is required to standardize is then added, care being taken to avoid loss by effervescence, and the beaker is set aside until the reaction is finished. The solution is then boiled for

a short time to expel any dissolved CO_2, small amounts of distilled water being added to balance loss by evaporation during the heating and thus prevent undue concentration. The solution, which should be quite clear, is then carefully decanted, and the beaker and the residual Iceland Spar washed several times with distilled water, and finally dried at a temperature of 110° C. in an air oven ; the beaker is then weighed. The loss in weight represents the amount of Iceland Spar required to neutralize the given volume of HCl, and the acid solution can then be standardized. For example :

Suppose 20 c.c. of the HCl solution were taken, and that the weight of Iceland Spar converted into calcium chloride was 1·60 grams.

Then, 1·60 grams of $CaCO_3$ are equivalent to 20 c.c. of HCl solution,

∴ 1 gram of $CaCO_3$ is equivalent to $\frac{20}{1·60}$, or 12·5 c.c. of HCl.

Thus, since 1 gram of $CaCO_3$ will neutralize exactly 20 c.c. of N.HCl, it follows that 20 — 12·5, or 7·5 c.c., of distilled water must be added to every 12·5 c.c. of the acid solution to make it accurately normal ; i.e. 600 c.c. of water must be added to 1 litre of the HCl solution.
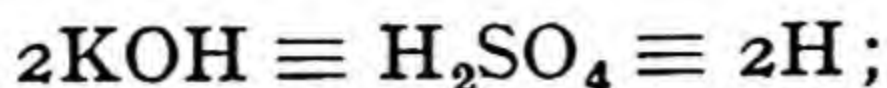
(b) *Standardization of HCl by the Constant Boiling Solution Method.* When hydrogen chloride is dissolved in water it does not obey Henry's Law, for its solubility in water is by no means proportional to the pressure ; the reason being that a change in the compound has occurred in virtue of which it is dissociated into free hydrogen and chlorine ions. When a concentrated solution of hydrochloric acid is boiled, gaseous HCl is given off unchanged until the temperature reaches 110° C., when the acid distils over unchanged, and the distillate contains 8 molecules of H_2O to 1 molecule of HCl, corresponding to a 20·2% solution. Moreover, when a dilute solution of hydrochloric acid is boiled, water is given off until the temperature reaches 110° C., when the solution distils unchanged with the same percentage composition, 20·2. In consequence, by distilling any solution of hydrochloric acid, a 20·2% solution of HCl is obtained, and this can then be diluted to the desired strength.

(c) *The Gaseous HCl Method of Standardization.* A very accurate method of preparing a standard solution of HCl is

to take a known weight of distilled water, pass into it pure, dry hydrogen chloride, and then weigh the amount of gas absorbed. The strength of the solution thus obtained may be expressed as a percentage, and diluted to any required strength.

TYPICAL VOLUMETRIC DETERMINATIONS

17. The manner of determining the strength of any simple acid or alkaline solution by means of a base or acid of known strength will now be quite familiar, and we can apply these methods to more complex estimations.

TO DETERMINE THE NUMBER OF MOLECULES OF WATER OF CRYSTALLIZATION IN HYDRATED SODIUM CARBONATE

About 250 c.c. of approximately 3% sodium carbonate solution are prepared, the crystals being weighed accurately and made up to the required volume in a graduated flask. Aliquot portions of this solution are then titrated with $0.1N.HCl$, using methyl orange as indicator ; several concordant results are obtained and the weight of pure anhydrous Na_2CO_3 per litre of solution calculated in the usual way. The number of molecules of water of crystallization in the hydrated carbonate can then be determined in the following manner :

Let m_1 be the weight of hydrated Na_2CO_3 in one litre of solution, and let m_2 be the weight of anhydrous Na_2CO_3 per litre, as determined by the titration with $0.1N.HCl$.

Then, $$\frac{\text{Molecular weight of hydrated salt}}{\text{Molecular weight of anhydrous salt}} = \frac{m_1}{m_2} ;$$

i.e. $$\frac{Na_2CO_3.xH_2O}{Na_2CO_3} \quad . \quad . \quad . \quad . \quad . \quad . = \frac{m_1}{m_2} ;$$

or, $$\frac{106 + 18x}{106} \quad . \quad . \quad . \quad . \quad . \quad . \quad . = \frac{m_1}{m_2} ,$$

where x represents the number of molecules of water of crystallization associated with one molecule of Na_2CO_3.

For example, in an experiment, 1.79 grams of hydrated salt were made up, after solution in distilled water, to 250 c.c.

Thus 1 litre of the solution contained 1.79×4, or 7.16 grams of the hydrated salt.

25 c.c. of the solution were exactly neutralized by 12.5 c.c.

of o·1N.HCl, thus, the normality of the carbonate solution is
o·1N. $\times \dfrac{12 \cdot 5}{25}$, or o·05N.

Therefore 1 litre of this solution will contain $53 \times 0 \cdot 05$, or 2·65 grams of Na_2CO_3.

Substituting for m_1 and m_2, we have

$$\frac{106 + 18x}{106} = \frac{2 \cdot 65}{7 \cdot 16};$$

i.e. $x = 10.$

Therefore, the formula of hydrated sodium carbonate is $Na_2CO_3, 10H_2O$.

18. To Determine the Strength of a Solution of Barium Chloride. The strength of a solution of barium chloride, and of any other soluble metallic salt which forms an insoluble carbonate, may be readily determined by adding a known excess of sodium carbonate solution (standard) to precipitate all the metal as carbonate, and then titrating the residual sodium carbonate with standard acid.

The reaction is as follows :

$$BaCl_2 \;\rightleftharpoons\; \overset{++}{Ba} + \overset{-}{Cl} + \overset{-}{Cl}$$

$$Na_2CO_3 \;\rightleftharpoons\; \overset{=}{CO_3} + \overset{+}{Na} + \overset{+}{Na}$$

$$\downarrow$$

$$BaCO_3$$
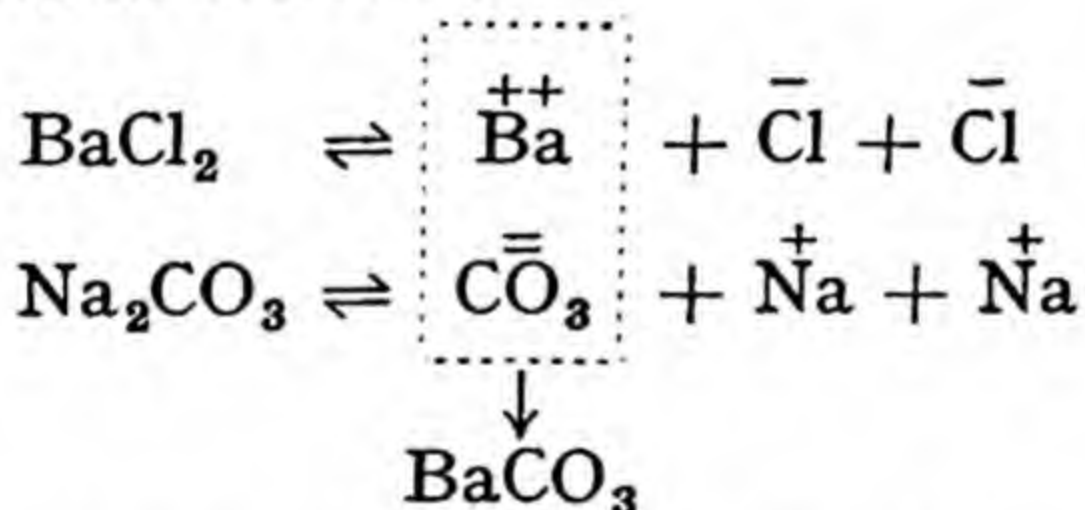
Method. To 25 c.c. of the solution of barium chloride is added more than sufficient o·1N.Na_2CO_3 than would be required to precipitate all the barium as carbonate (say x c.c. of o·1N.Na_2CO_3). The solution is then stirred thoroughly, filtered, and washed with distilled water ; the combined filtrate and washings are then titrated with standard acid, using methyl orange as the indicator. (It is preferable to make up the combined filtrate and washings to a convenient volume, and to titrate aliquot portions of this solution.)

Let the number of c.c. of standard acid (decinormal, of course) required to neutralize the excess Na_2CO_3 in 25 c.c. of the solution, be y.

Then the volume of o·1N.Na_2CO_3 used in precipitating the barium as carbonate is $(x - y)$ c.c.

Then, $Na_2CO_3 \equiv BaCl_2.$
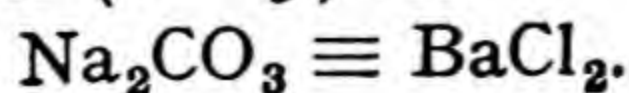
Therefore, 106 grams of Na_2CO_3 are equivalent to 208 grams of $BaCl_2$.

Therefore, 53 grams of Na_2CO_3 are equivalent to 104 grams of $BaCl_2$.

Therefore 1 litre of $0.1N.Na_2CO_3$ is equivalent to 10.4 grams of $BaCl_2$.

Therefore $(x - y)$ c.c. of $0.1N.Na_2CO_3$ are equivalent to $0.0104 (x - y)$ grams $BaCl_2$.

Thus, 25 c.c. of the $BaCl_2$ solution contain $0.0104 (x - y)$ grams of $BaCl_2$, and the strength of the solution can then be expressed in grams per c.c. or in grams per litre.

19. To DETERMINE THE STRENGTH OF A SOLUTION OF COPPER SULPHATE. In this case the principle is the same as in the previous determination. A known excess of standard NaOH is used to precipitate all the copper as hydroxide, and the residual NaOH is titrated with standard acid. The reaction is represented by the equation :

$$CuSO_4 \rightleftharpoons \overset{++}{Cu} + S\overset{=}{O}_4$$
$$2NaOH \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{+}{Na} + \overset{+}{Na}$$
$$\downarrow$$
$$Cu(OH)_2$$
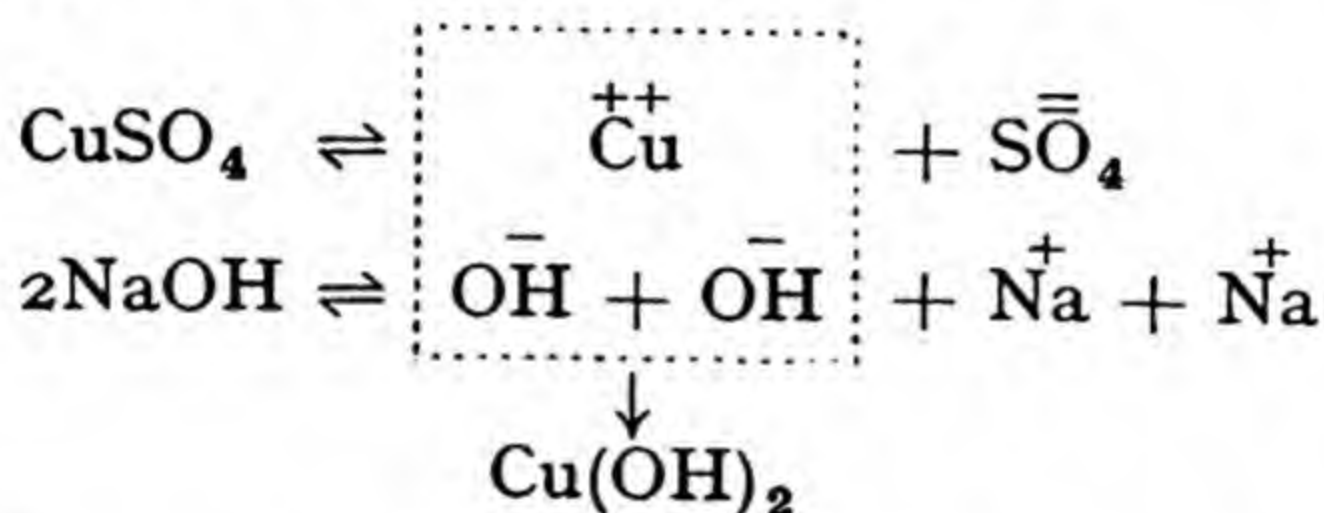
The calculation proceeds on the same lines as in the case of barium chloride.

Thus, if x c.c. of $0.1N.NaOH$ are added to 25 c.c. of the $CuSO_4$ solution and y c.c. of $0.1N.$ acid are required to neutralize the excess NaOH, then the volume of $0.1N.NaOH$ required to precipitate all the copper as hydroxide is $(x-y)$ c.c.

Then, since $2NaOH \equiv CuSO_4.$

it follows that 1 litre of $0.1N.NaOH$ is equivalent to $\dfrac{16.0}{2}$, or 8.0 grams, of copper sulphate.

Therefore, $(x - y)$ c.c. of $0.1N.NaOH \equiv 0.008 (x - y)$ grams of $CuSO_4$, which will be contained in 25 c.c. of the copper sulphate solution.

20. THE DETERMINATION OF THE CHEMICAL EQUIVALENT OF A METAL. If a metal is soluble in an acid, its equivalent weight may be determined accurately by dissolving the metal in a measured excess of standard acid, and then titrating the

residual acid. The difference between the total acid and the residual acid is the amount of acid used in dissolving the given weight of the metal, the equivalent of which is then calculated.

For example, to determine the chemical equivalent of magnesium, the procedure would be as follows :

About 0·4 gram of thoroughly cleaned magnesium ribbon is weighed accurately and dissolved in exactly 100 c.c. of normal sulphuric acid. The magnesium dissolves in part of the acid, forming magnesium sulphate and hydrogen according to the equation :

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$
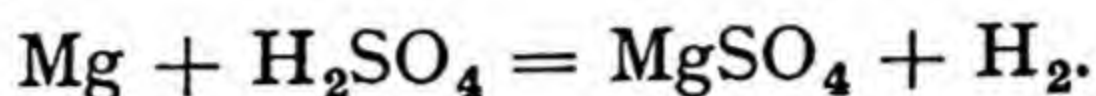
The residual acid is then titrated with normal NaOH, using litmus as the indicator.

Suppose that x c.c. of N.NaOH are required to neutralize the residual acid, then $(100 - x)$ c.c. of $N.H_2SO_4$ have been used in reacting with the known weight of magnesium. Since the chemical equivalent of H_2SO_4 is half the molecular weight, i.e. 49, the weight of magnesium which will react with the equivalent weight of H_2SO_4 (i.e. 1 litre of normal acid) can be easily calculated.

This volumetric method of determining the chemical equivalent of a metal can be employed with zinc, aluminium, tin, and iron, using either normal HCl or H_2SO_4. The method might be employed with copper and normal HNO_3, though, in this case, the blue colour of the copper nitrate formed in the reaction would render the change of colour of the indicator rather difficult to detect accurately when titrating the residual acid.

21. THE DETERMINATION OF THE CHEMICAL EQUIVALENT OF AN INSOLUBLE BASE. The chemical equivalents of insoluble bases such as ZnO, MgO, CuO, etc., may be accurately determined in a similar manner by dissolving a known weight of the base in a given volume of standard acid, determining the residual acid with standard sodium hydroxide, using litmus as the indicator, and then calculating the weight of insoluble base which has been neutralized by the equivalent weight of the acid.

For example, the chemical equivalent of zinc oxide would be determined as follows :

About 1 gram of the oxide is weighed accurately and treated with exactly 100 c.c. of normal hydrochloric acid

(this being the acid in which zinc oxide dissolves most readily). When the reaction

$$ZnO + 2HCl = ZnCl_2 + H_2O$$
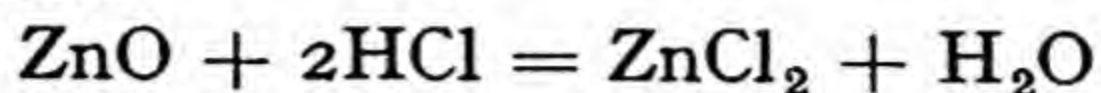
has been completed, the excess acid is titrated with normal caustic soda, using litmus as the indicator.

Suppose the mean of three concordant titrations gives x c.c. of N.NaOH as the volume required to neutralize the excess acid, then $(100 - x)$ c.c. of N.HCl have been used in neutralizing the known weight of base. The weight of base which will react with the chemical equivalent of HCl (36·5 grams) can then be deduced.

22. THE DETERMINATION OF A MIXTURE OF SODIUM CARBONATE AND BICARBONATE. The method is based upon the fact that sodium carbonate when titrated with acids behaves differently with phenolphthalein than is expected.

When *phenolphthalein* is the indicator 'equivalence' is indicated when the carbonate has all been converted to the bicarbonate :

$$Na_2CO_3 + HCl = NaCl + NaHCO_3.$$
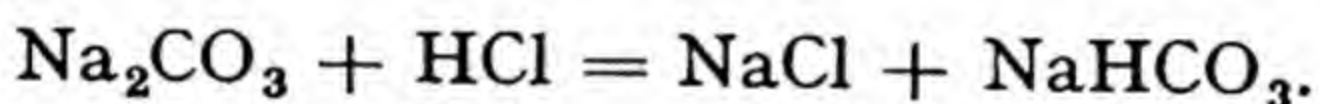
When, however, *methyl orange* is the indicator, 'equivalence' is indicated when the carbonate has been completely decomposed into carbon dioxide and water :

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$
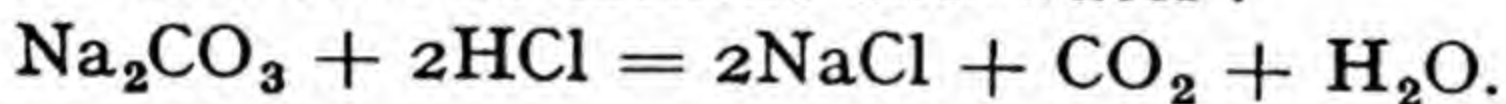
Method. A known weight of the mixture is dissolved in distilled water and diluted to a suitable volume. Aliquot portions of the solution are titrated with 0·1N.HCl in the presence of phenolphthalein, the acid being run in from the burette until the pink colour of the phenolphthalein is discharged. Suppose that the mean volume of 0·1N.HCl required to effect this is x c.c. :

One drop of methyl orange is then added to the solution and the titration continued until the end-point of the reaction is indicated by the colour change of the methyl orange. Suppose the mean volume of 0·1N.HCl required to be y c.c. :

Then, since x c.c. of acid are required to turn all the carbonate into bicarbonate, the amount of sodium carbonate in the solution will be represented by $2x$ c.c. of 0·1N.HCl.

The total alkali in the solution will be represented by

$$(x + y) \text{ c.c. of } 0\cdot1N.HCl.$$

Therefore, the bicarbonate will be represented by

$$(x + y - 2x), \text{ or } (y - x) \text{ c.c. of } 0\cdot1N.HCl.$$

For example, suppose that 9·08 grams of the mixture were made up to 1 litre with distilled water, and that 50 c.c. of this solution required, as a mean of three titrations, 23·0 c.c. of 0·1N.HCl to indicate ' equivalence ' with the phenolphthalein, and an addition of a further 48·0 c.c. of the same acid to effect the colour change with the methyl orange :

Then the amount of Na_2CO_3 in 50 c.c. of the solution will be represented by (23·0 × 2), or 46·0 c.c., of 0·1N.HCl.

Now 1 litre of 0·1N.HCl is equivalent to 5.3 grams of Na_2CO_3.

Therefore 46·0 c.c. of 0·1N.HCl is equivalent to 0·0053 × 46, or *0·244 gram Na_2CO_3*.

Similarly 1 litre of 0·1N.HCl is equivalent to 8·4 grams of $NaHCO_3$,

Therefore 25·0 c.c. of 0·1N.HCl is equivalent to 0·0084 × (48 — 23), or *0·21 grams of $NaHCO_3$*.

Thus, 1 litre of the alkaline solution contains 0·244 × 20, or *4·88 grams, of Na_2CO_3*, and 0·21 × 20, or *4·20 grams of $NaHCO_3$*.

The composition of the mixture may also be expressed as a percentage if desired.

23. THE ESTIMATION OF CAUSTIC SODA AND SODIUM CARBONATE IN SODA ASH. The percentage composition of soda ash, or of any mixture of caustic soda and sodium carbonate, may also be determined by making use of the behaviour of sodium carbonate toward phenolphthalein and methyl orange.

Method. A quantity of the soda ash is weighed accurately, dissolved in water, and diluted to suitable volume. Aliquot portions of the solution are titrated with N.HCl in the presence of phenolphthalein, ' equivalence ' being indicated when the sodium hydroxide has been completely neutralized and the sodium carbonate all converted into the bicarbonate according to the reactions :

(a) $NaOH + HCl = NaCl + H_2O$,

(b) $Na_2CO_3 + HCl = NaCl + NaHCO_3$.
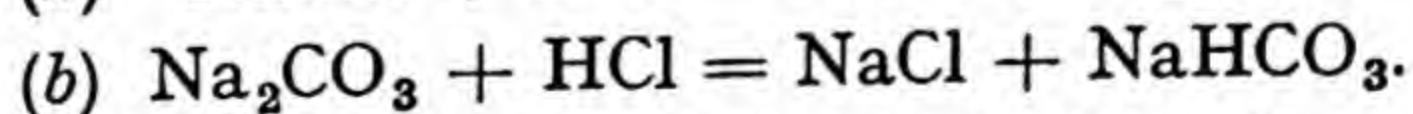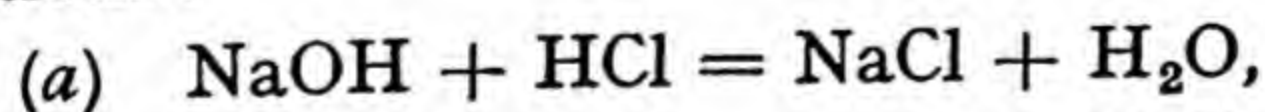
Let the mean volume of N.HCl required to effect these two changes be x c.c.

One drop of methyl orange is then added to the solution and the titration is continued until ' equivalence ' is indicated. Let the mean volume of N.HCl required for this final titration be y c.c. :

Then the total alkali will be represented by $(x + y)$ c.c.

of N.HCl, and, since y c.c. of the acid were required to neutralize the sodium bicarbonate, it follows that $2y$ c.c. of N.HCl will represent the amount of sodium carbonate in the solution. Therefore, the NaOH will be represented by $(x + y - 2y)$ or $(x - y)$ c.c. of N.HCl.

For example, in an experiment 87·5 c.c. of N.HCl were required to discharge the pink colour of phenolphthalein for 50 c.c. of a soda ash solution containing a known weight of the mixture. An additional 11·0 c.c. of N.HCl were required to indicate neutrality with methyl orange.

Then the amount of NaOH is equivalent to (87·5 − 11), or 76·5 c.c. of N.HCl.

∴ since 1 litre of N.HCl is equivalent to 40 grams of NaOH, 76·5 c.c of N.HCl is equivalent to 0·04 × 76·5, or *3·06 gram of NaOH*.

Similarly, the amount of Na_2CO_3 is equivalent to (2 × 11·0) or 22·0 c.c. N.HCl, and 1 litre of N.HCl is equivalent to 53 grams of Na_2CO_3.

∴ 22·0 c.c. of N.HCl is equivalent to 0·053 × 22·0, or *11·66 grams of Na_2CO_3*.

The percentage composition of the mixture may then be obtained in the usual way.

24. THE DETERMINATION OF TWO ACIDS IN A MIXTURE WHEN THE TOTAL AMOUNT OF ACID IS KNOWN. This estimation depends upon the difference between the chemical equivalents of the two acids, and the greater that difference is the higher is the degree of accuracy of the determination.

Suppose that it is required to determine the proportions of nitric and hydrochloric acids in a solution containing a known weight of the total acid. Aliquot portions of the solution are titrated with standard alkali, litmus being used as the indicator, and the mean volume of the standard alkali required to effect complete neutralization obtained.

The proportions of HCl and HNO_3 respectively in the solution are then calculated as follows :

Let x be the weight of HNO_3 in 1 litre of the solution, and

Let y be the weight of HCl in 1 litre of the solution. Then the amounts of each acid are obtained from the following simultaneous equations, using NaOH as the standard alkali :

$$x + y = m_1 \quad \text{................................}(a)$$

$$\frac{40x}{63} + \frac{40y}{36\cdot5} = m_2 \quad \text{................................}(b)$$

where m_1 denotes the weight of the mixed acids in 1 litre of the original solution, and m_2 the weight of NaOH required to neutralize 1 litre of the acid solution (determined by the titration). In (b) 40, 63, and 36·5 are the chemical equivalents of NaOH, HNO_3, and HCl respectively.

For example, suppose that the total acid in a solution containing a mixture of HNO_3, and HCl is 10·0 grams per litre, and that 25 c.c. of this solution need a mean titration of 51·0 c.c. of decinormal NaOH for complete neutralization.

Then 1 litre of the acid solution is equivalent to 51·0 × 40, or 2040 c.c. of 0·1N.NaOH ; i.e. 40 × 2·04, or 8·16 grams of NaOH.

Then
$$x + y = 10 \ldots\ldots\ldots\ldots\ldots(a)$$

$$\frac{40x}{63} + \frac{40y}{36·5} = 8·16 \ldots\ldots\ldots\ldots(b)$$

From which
$$x = 6·08, \ y = 3·92.$$

Therefore, the acid solution contains *6·08 grams of HNO₃*, and *3·92 grams of HCl* per litre.

This method can be employed with other acids, but it must be remembered that the chemical equivalents of the acids in question must not be too near each other in value, as the error in the calculation of results increases as the equivalent weights of the acids used approach each other.

25. TO DETERMINE THE AMOUNTS OF CAUSTIC SODA AND CAUSTIC POTASH IN A MIXTURE WHEN THE TOTAL ALKALI IS KNOWN. In this determination the procedure is similar to that of the previous experiment, standard acid being used to determine the total alkali solution, and the respective amounts of each base calculated in the same way. Using standard HCl as the titrating acid, the determination would be calculated from the simultaneous equations :

$$x + y = m_1 \ldots\ldots\ldots\ldots\ldots(a)$$

$$\frac{36·5x}{40} + \frac{36·5y}{56} = m_2 \ldots\ldots\ldots\ldots(b)$$

where x and y are the weights of NaOH and KOH respectively in 1 litre of the alkali solution : m_1 is the weight of total alkali per litre of solution, and m_2 is the weight of HCl required to neutralize 1 litre of the alkaline solution (determined by titration with litmus as indicator).

For example, suppose that a solution of NaOH and KOH containing 9·60 grams of total alkali per litre were titrated

with 0·1N.HCl, 25 c.c. of which required 12·3 c.c. of the alkaline solution for complete neutralization:

Then 1 litre of the alkaline solution is equivalent to $25 \times \dfrac{1000}{12 \cdot 3}$, or 2032·5 c.c., of 0·1N.HCl; i.e. 3·65 × 2·0325, or 7·42 grams, of HCl.

Then

$$x + y = 9 \cdot 60 \quad \text{.........................} (a)$$
$$\frac{36 \cdot 5x}{40} + \frac{36 \cdot 5y}{56} = 7 \cdot 42 \quad \text{.....................} (b)$$

From which $x = 4 \cdot 46, \quad y = 5 \cdot 14.$

Therefore, the alkaline solution contains *4·46 grams of NaOH*, and *5·14 grams of KOH per litre*.

26. TO DETERMINE THE AMOUNTS OF SODIUM CARBONATE AND POTASSIUM CARBONATE IN A MIXTURE, THE TOTAL CARBONATE BEING KNOWN. In this determination, again, the same method, based upon the difference in equivalents of the two carbonates, is employed. Decinormal H_2SO_4 can be used for the titration in the presence of methyl orange.

The simultaneous equations for calculating the respective amounts of each carbonate in the mixture would be:

$$x + y = m_1 \quad \text{...........................} (a)$$
$$\frac{49x}{53} + \frac{49y}{69} = m_2 \quad \text{........................} (b)$$

where x and y are the weights of Na_2CO_3 and K_2CO_3 respectively in 1 litre of the alkaline solution; m_1 the weight of total carbonate in 1 litre of the solution, and m_2 the weight of H_2SO_4 required to neutralize 1 litre of the carbonate solution. 53, 69, and 49 are the respective equivalents of Na_2CO_3, K_2CO_3 and H_2SO_4.

27. THE DETERMINATION OF BORAX. Borax, $Na_2B_4O_7$. $10H_2O$, being the salt of a strong base (NaOH) and a weak acid (pyroboric acid), reacts strongly alkaline in solution as the result of hydrolysis. It may be determined, therefore, by titrating with standard HCl, using methyl orange as the indicator. The reaction takes place according to the equation:

$$Na_2B_4O_7 . 10H_2O + 2HCl = 2NaCl + 4H_3BO_3 + 5H_2O.$$
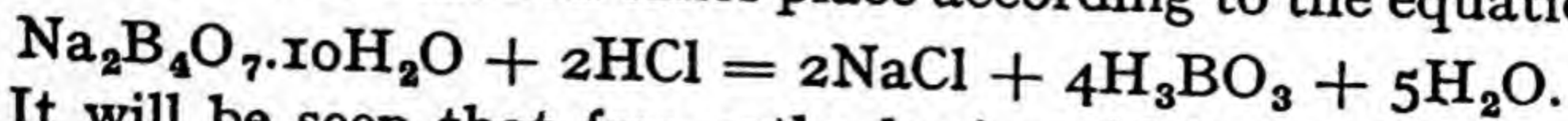
It will be seen that free ortho-boric acid is formed in the reaction, but, as methyl orange is a fairly strong base, the feebly acid character of the ortho-boric acid will have no effect

3

on the indicator, or, at any rate, not to any measurable extent (see § 142).

In this reaction

$$Na_2B_4O_7.10H_2O \equiv 2HCl \equiv 2H.$$
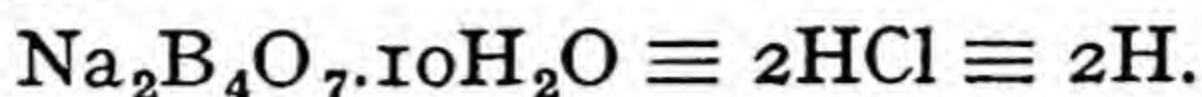
Therefore the chemical equivalent of hydrated borax is $\frac{382}{2}$, or 191; and 1 litre of 0·1N.HCl will be equivalent to 19·1 grams of $Na_2B_4O_7.10H_2O$.

For example, in an experiment 4·20 grams of crude borax were dissolved in water and diluted to 250 c.c. As a mean of three titrations, 25 c.c. of this solution required 20·5 c.c. of 0·1N.HCl to effect a colour change with methyl orange.

Then, 1 litre of 0·1N.HCl = 19·1 grams of $Na_2B_4O_7.10H_2O$,

$\therefore$ 20·5 c.c. ,, ,, ,, $\equiv 19·1 \times \frac{20·5}{1000}$, or 0·39 gram, of $Na_2B_4O_7.10H_2O$.

Now, this weight of borax is contained in 25 c.c. of the solution of crude borax, therefore 250 c.c. of the solution will contain 3·9 grams of pure borax.

Thus, the percentage of pure borax in the sample is $\frac{390}{42}$, or 93%.

A check can be obtained on the result thus obtained by adding a little phenolphthalein to the solution and titrating the free ortho-boric acid (liberated in the titration with HCl) by decinormal NaOH. The 'end-point,' however, is unsatisfactory unless a large quantity of glycerol (or certain other polyhydric alcohols) be present in the solution; why polyhydric alcohols should render the 'end-point' more definite is not yet understood, but glycerol, in particular, possesses this peculiar property. The reaction may be represented by the equation:

$$4H_3BO_3 + 4NaOH = 4NaBO_2 + 8H_2O.$$
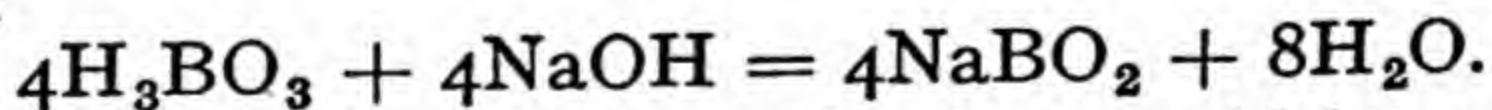
It will be noticed that the ortho-boric acid is so weak that it is only partially neutralized, forming sodium metaborate and not the ordinary borate.

Here $4NaOH \equiv 4H_3BO_3 \equiv Na_2B_4O_7.10H_2O$.

Thus, 1 litre of 0·1N.NaOH will be equivalent to $\frac{38·2}{4}$, or 9·55 grams of borax. This is exactly half the chemical equivalent used in the first reaction.

In carrying out this second determination, there is one

*important caution which must be observed : the NaOH must be
tested to see that it is free from sodium carbonate, since not only
would the CO_2 liberated affect the phenolphthalein but the sodium
carbonate would react with the ortho-boric acid, forming borax.*

For example, after titrating the borax in the first experi-
ment with o·1N.HCl, a few drops of phenolphthalein and
about 30 grams of pure glycerol were added to the solution
containing the liberated ortho-boric acid. As a mean of three
titrations, it was found that 41·2 c.c. of o·1N.NaOH were
required to neutralize the H_3BO_3 liberated from 25 c.c. of
borax solution.

Then,

1 litre of o·1N.NaOH $\equiv$ 9·55 grams of $Na_2B_4O_7.10H_2O$.

Therefore, 41·2 c.c. of o·1N.NaOH $\equiv$ 9·55 $\times \dfrac{41·2}{1000}$, or 0·39

gram, of $Na_2B_4O_7.10H_2O$.

This amount of borax is contained in 25 c.c. of the original
solution ; therefore, 250 c.c. will contain 3·9 grams of pure
borax.

Thus, the percentage of pure borax in the sample is $\dfrac{390}{4·2}$,
or 93%.

28. THE DETERMINATION OF AMMONIUM SALTS. In the
estimation of ammonia in ammonium salts one of two alter-
native methods may be employed. They are both based
upon the fact that any ammonium salt when heated with a
caustic alkali evolves ammonia gas.

Method 1. The 'Direct' Method.—In this determination a
known weight of ammonium salt is boiled with a measured
excess of standard NaOH solution until the evolution of
ammonia is completed. The residual NaOH is then titrated
with standard acid, and the difference between the original
and final amounts of NaOH will represent the given weight
of ammonium salt ; e.g. *the estimation of Ammonia in
Ammonium Chloride.*

About 1 gram of ammonium chloride is weighed accurately
in a small flask ; 250 c.c. of o·1N.NaOH are then added and
the solution boiled until no more ammonia is evolved ; this
can be tested by means of turmeric paper, which is turned
brown by ammonia. The solution is then allowed to cool,
diluted to a suitable volume, and aliquot portions of the
diluted solution are titrated with o·1N·HCl in the presence of
litmus.

The following are the results of an actual experiment :

Weight of NH_4Cl = 1·07 grams.

Volume of 0·1N.NaOH added to the ammonium chloride = 250 c.c.

After all the ammonia had been expelled the residual solution was diluted to 250 c.c., and portions of 75 c.c. were titrated with 0·1N.HCl.

As a mean value of three titrations it was found that 15·0 c.c. of the acid were required.

Thus, the whole 250 c.c. would require $15 \times \dfrac{250}{75}$, or 50 c.c., of 0·1N.HCl.

Therefore, 50 c.c. of 0·1N.NaOH were left, and (250 − 50), or 200 c.c., of the 0·1N.NaOH were needed to expel all the ammonia from 1·07 grams of ammonium chloride.

Now, $$\underset{40}{NaOH} \equiv \underset{17}{HCl} \equiv NH_3$$

Therefore, 1 litre of 0·1N.NaOH is equivalent to 1·7 grams of NH_3.

Therefore 200 c.c., of 0·1N.NaOH is equivalent to 0·34 gram of NH_3.

Therefore, the percentage of ammonia in ammonium chloride is $\dfrac{34}{1·07}$, or *31·8%*.

Method 2. The ' Indirect' Method.—In this determination the known weight of ammonium salt is boiled with excess of caustic soda of unknown strength and the ammonia evolved in the reaction is absorbed in a known volume of standard acid solution. When the reaction is complete the residual acid is titrated with standard alkali, using litmus or cochineal as the indicator. The difference between the original and residual acid represents the amount of ammonia in the ammonium salt. In the case of ammonium chloride, and where sulphuric acid is used to absorb the ammonia, the reactions are as follows :

(a) $NH_4Cl + NaOH = NaCl + NH_3 + H_2O$,

(b) $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$.
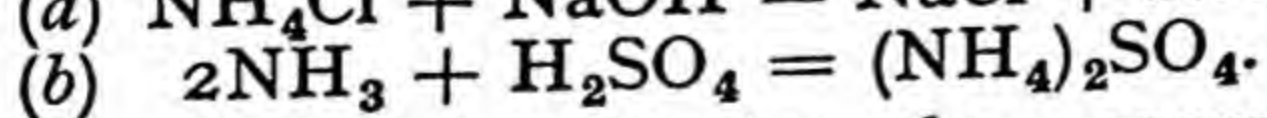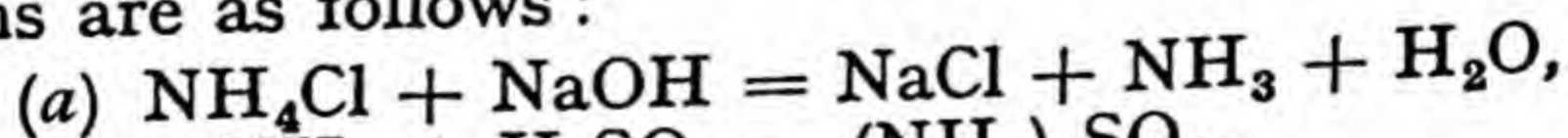
In the actual determination the apparatus is assembled as shown in Fig. 3. The flask A is fitted with a two-holed rubber cork, which carries a tap-funnel and a delivery tube having a bulb blown at C in order to prevent the solution in the flask B from ' sucking back '. About 1 gram of pure ammonium chloride is weighed accurately and dissolved

in 50 c.c. of distilled water in the flask A; the tap-funnel is filled with an approximately 25% solution of caustic soda, and 100 c.c. of normal H_2SO_4 are placed in the flask B, which stands in a basin of cold water. The ammonium chloride solution in A is heated *just* to the boiling point, whilst the caustic soda is allowed to run in a drop at a time. When all the caustic soda solution has been used, the tap of the funnel is closed and the solution boiled for about fifteen minutes. When this operation is finished, the delivery tube is washed with distilled water, and the washings added to the contents of the flask B; this solution is then transferred to a 200 c.c.
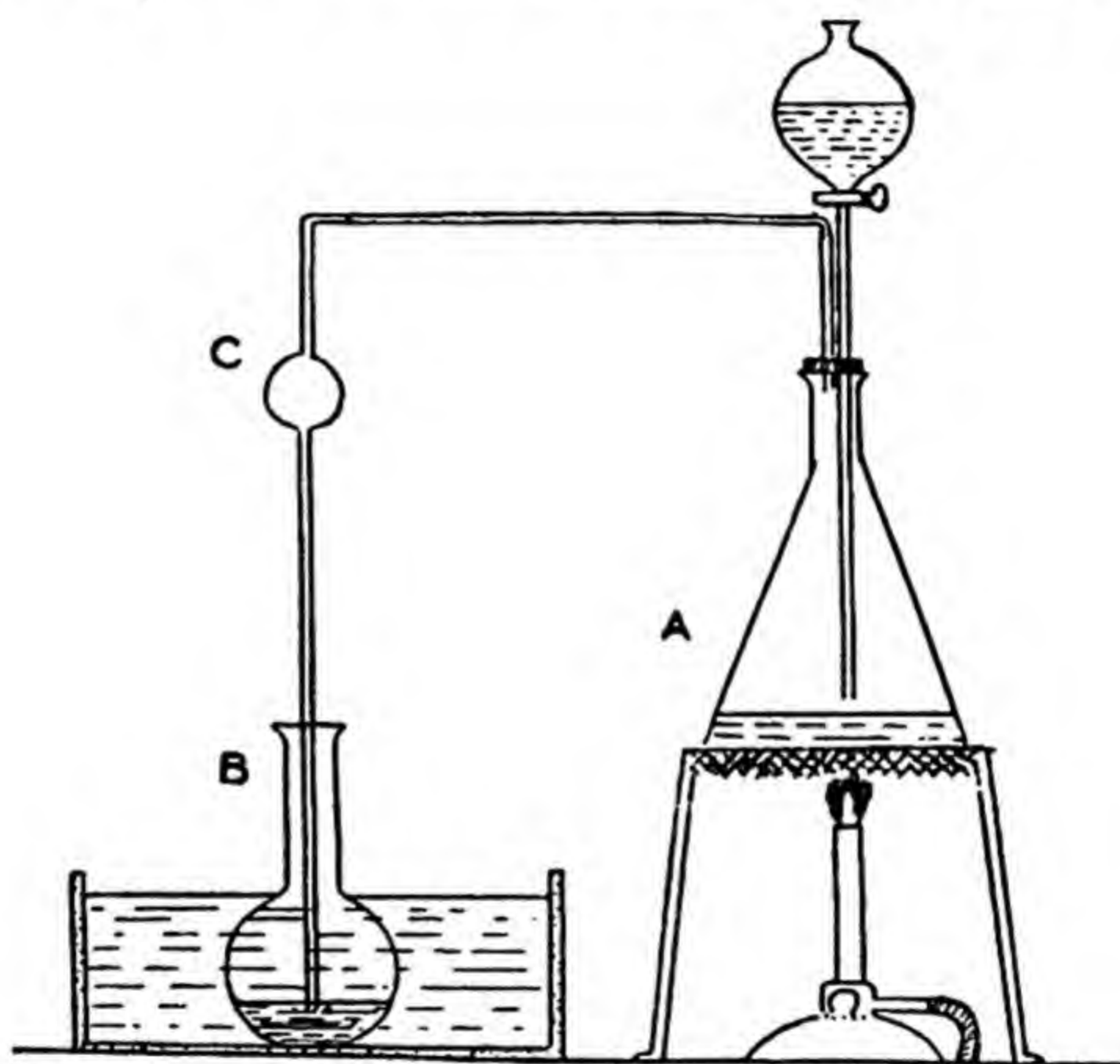
FIG. 3

ESTIMATION OF AMMONIUM SALTS

graduated flask; the flask B is washed thoroughly with distilled water, and the washings are added to the solution, which is then made up to the mark with more distilled water. Aliquot portions of the acid solution are then titrated with normal NaOH, using litmus as the indicator. The percentage of ammonia in the ammonium salt is then calculated.

For example, suppose that the weight of ammonium chloride was 1·026 grams, and that, as a mean of three titrations, 20·2 c.c. of the N.NaOH were needed to neutralize 50 c.c. of the acid solution:

Then, 200 c.c. of the acid solution would require 20·2 × 4, or 80·8 c.c., of N.NaOH for complete neutralization.

Therefore, the volume of $N.H_2SO_4$ neutralized by the evolved ammonia is (100 − 80·8), or 19·2 c.c., and this is equivalent to 19·2 c.c. of normal ammonia solution.

But 19·2 c.c. of normal NH_3 solution contain 19·2 × 0·017 grams of NH_3.

Therefore the percentage of ammonia in ammonium chloride is

$$\frac{19 \cdot 2 \times 0 \cdot 017}{1 \cdot 026} \times 100, \text{ or } 31 \cdot 8\%.$$

N.B.—In both these methods for the estimation of ammonia, phenolphthalein must never be employed, since its ammonium salt is largely hydrolyzed in solution, and the ' end-point ' of the reaction would therefore be indicated prematurely (see § 142).

29. The Determination of Ortho-Phosphoric Acid. Ortho-phosphoric acid, H_3PO_4, is a tribasic acid of moderate strength which forms three series of salts. Its behaviour toward indicators, however, is rather striking.

(a) Then *methyl orange* is employed as the indicator, the colour change occurs when *one* of the three hydrogen atoms has been replaced by sodium.

Thus, $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$;

or, according to the ionic hypothesis :

$$H_3PO_4 \rightleftharpoons \overset{+}{H} + H_2\overset{-}{PO_4}$$

$$NaOH \rightleftharpoons \overset{-}{OH} + \overset{+}{Na}$$

$$\Updownarrow$$

$$H_2O$$

(b) When, however, *phenolphthalein* is used as an indicator, the colour change corresponds to the replacement of *two* of the hydrogen atoms.

Thus, $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$;

or, depicting the reaction ionically :

$$H_3PO_4 \rightleftharpoons \overset{+}{H} + H_2\overset{-}{PO_4}$$

$$\overset{+}{H} + H\overset{=}{PO_4}$$

$$2NaOH \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{+}{Na} + \overset{+}{Na}$$

$$\Updownarrow$$

$$2H_2O$$

(c) No satisfactory indicator has yet been found which will indicate the complete neutralization of ortho-phosphoric acid according to the equation :

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O.$$

or,

$$H_3PO_4 \rightleftharpoons \quad \overset{+}{H} \quad + H_2\overset{-}{PO_4}$$
$$\overset{+}{H} \quad + H\overset{=}{PO_4}$$
$$\overset{+}{H} \quad + \overset{\equiv}{PO_4}$$

$$3NaOH \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{-}{OH} \quad + \overset{+}{Na} + \overset{+}{Na} + \overset{+}{Na}$$

$$3H_2O$$

The reason for this will be found in § 146 on the behaviour of polybasic acids toward indicators, and the problem is still further complicated by the fact that Na_3PO_4 is strongly alkaline in solution, being easily decomposed by such weak acids as carbonic acid.

Thus, in determining the strength of a solution containing ortho-phosphoric acid, where *methyl* orange is employed as the indicator, *one* molecule of the acid is equivalent to *one* molecule of NaOH.

Suppose that 25 c.c. of the centinormal NaOH required, as a mean of three titrations, 28·5 c.c. of the acid solution to effect the colour change with methyl orange :

Then, since 1 litre of 0·01N.NaOH is equivalent to 1 litre of 0·01 *molar* H_3PO_4, the strength of the acid solution will be $\frac{25·0}{28·5} \times$ 0·01 molar ; i.e. 1 litre of the acid solution contains 0·98 $\times \frac{25·0}{28·5}$, or *0·86 gram, of H_3PO_4.*

On the other hand, if *phenolphthalein* be employed as the indicator, *one* molecule of the acid will be equivalent to *two* molecules of sodium hydroxide.

For example, with the same solution of ortho-phosphoric acid as in the previous determination it was found that, as a mean of three titrations, 50 c.c. of the 0·01N.NaOH required 28·5 c.c. of the acid solution to discharge the pink colour of the phenolphthalein.

Then, since in this case, 1 litre of 0·01N.NaOH is equivalent

Therefore, the volume of $N.H_2SO_4$ neutralized by the evolved ammonia is $(100 - 80.8)$, or 19.2 c.c., and this is equivalent to 19.2 c.c. of normal ammonia solution.

But 19.2 c.c. of normal NH_3 solution contain 19.2×0.017 grams of NH_3.

Therefore the percentage of ammonia in ammonium chloride is

$$\frac{19.2 \times 0.017}{1.026} \times 100, \text{ or } 31.8\%.$$

N.B.—In both these methods for the estimation of ammonia, phenolphthalein must never be employed, since its ammonium salt is largely hydrolyzed in solution, and the ' end-point ' of the reaction would therefore be indicated prematurely (see § 142).

29. THE DETERMINATION OF ORTHO-PHOSPHORIC ACID. Ortho-phosphoric acid, H_3PO_4, is a tribasic acid of moderate strength which forms three series of salts. Its behaviour toward indicators, however, is rather striking.

(a) Then *methyl orange* is employed as the indicator, the colour change occurs when *one* of the three hydrogen atoms has been replaced by sodium.

Thus, $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$;
or, according to the ionic hypothesis :

$$H_3PO_4 \rightleftharpoons \overset{+}{H} + H_2\overset{-}{PO_4}$$
$$NaOH \rightleftharpoons \overset{-}{OH} + \overset{+}{Na}$$
$$\Updownarrow$$
$$H_2O$$

(b) When, however, *phenolphthalein* is used as an indicator, the colour change corresponds to the replacement of *two* of the hydrogen atoms.

Thus, $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$;
or, depicting the reaction ionically :

$$H_3PO_4 \rightleftharpoons \overset{+}{H} + H_2\overset{-}{PO_4}$$
$$\overset{+}{H} + H\overset{=}{PO_4}$$
$$2NaOH \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{+}{Na} + \overset{+}{Na}$$
$$\Updownarrow$$
$$2H_2O$$

(c) No satisfactory indicator has yet been found which will indicate the complete neutralization of ortho-phosphoric acid according to the equation :

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O.$$

or,

$$H_3PO_4 \rightleftharpoons \quad \overset{+}{H} \qquad + H_2\overset{-}{PO_4}$$
$$\overset{+}{H} \quad + H\overset{=}{PO_4}$$
$$\overset{+}{H} + \overset{\equiv}{PO_4}$$

$$3NaOH \rightleftharpoons \overset{-}{OH} + \overset{-}{OH} + \overset{-}{OH} \quad + \overset{+}{Na} + \overset{+}{Na} + \overset{+}{Na}$$

$$3H_2O$$

The reason for this will be found in § 146 on the behaviour of polybasic acids toward indicators, and the problem is still further complicated by the fact that Na_3PO_4 is strongly alkaline in solution, being easily decomposed by such weak acids as carbonic acid.

Thus, in determining the strength of a solution containing ortho-phosphoric acid, where *methyl* orange is employed as the indicator, *one* molecule of the acid is equivalent to *one* molecule of NaOH.

Suppose that 25 c.c. of the centinormal NaOH required, as a mean of three titrations, 28·5 c.c. of the acid solution to effect the colour change with methyl orange :

Then, since 1 litre of 0·01N.NaOH is equivalent to 1 litre of 0·01 *molar* H_3PO_4, the strength of the acid solution will be $\dfrac{25\cdot0}{28\cdot5} \times 0\cdot01$ molar ; i.e. 1 litre of the acid solution contains

$0\cdot98 \times \dfrac{25\cdot0}{28\cdot5}$, or *0·86 gram, of H_3PO_4.*

On the other hand, if *phenolphthalein* be employed as the indicator, *one* molecule of the acid will be equivalent to *two* molecules of sodium hydroxide.

For example, with the same solution of ortho-phosphoric acid as in the previous determination it was found that, as a mean of three titrations, 50 c.c. of the 0·01N.NaOH required 28·5 c.c. of the acid solution to discharge the pink colour of the phenolphthalein.

Then, since in this case, 1 litre of 0·01N.NaOH is equivalent

to 1 litre of 0·005 molar H_3PO_4, the strength of the acid solution will be $\frac{50·0}{25·8} \times 0·005$ molar; i.e. 1 litre of the acid solution contains $0·49 \times \frac{50·0}{28·5}$, or *0·86 gram, of H_3PO_4.*

30. THE ESTIMATION OF WEAK ORGANIC ACIDS. Weak organic acids can be estimated by titration with strong bases using *phenolphthalein* as the indicator. The base which is best adapted for this work is *Barium Hydroxide* solution (baryta water). Since the solid barium hydroxide has a limited solubility in water the solution should never be stronger than decinormal.

Since *one* molecule of barium hydroxide reacts with *two* molecules of HCl according to the equation :

$$Ba(OH)_2 + 2HCl = BaCl_2 + 2H_2O,$$
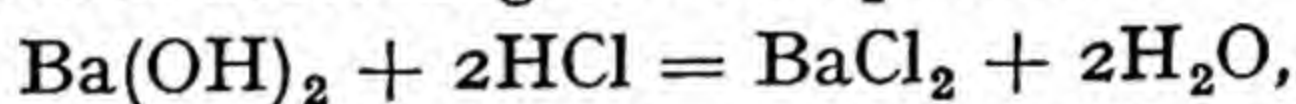
it follows that a normal solution of $Ba(OH)_2$ will be a semimolar solution, and a decinormal solution will therefore contain $\frac{17·1}{2}$, or 8·55 grams, per litre.

In using the $Ba(OH)_2$ solution, it should always be protected from the air, as it reacts with the atmospheric carbon dioxide forming insoluble barium carbonate :

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$
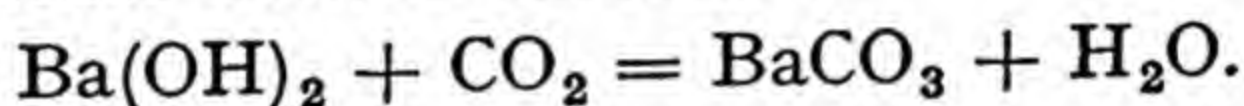
The Estimation of Succinic Acid. Succinic Acid, $(CH_2COOH)_2$, is a weak organic acid which reacts with sodium hydroxide according to the equation :

$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + 2NaOH = \begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix} + 2H_2O.$$
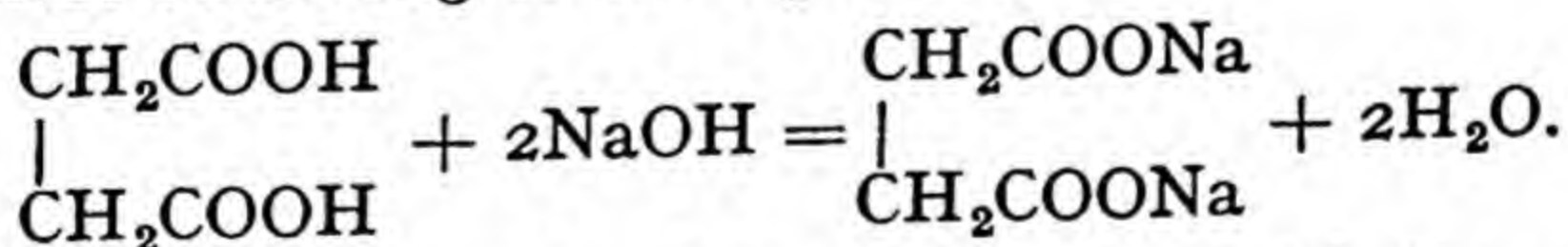
Thus, since *one* molecule of the acid reacts with *two* molecules of NaOH, the chemical equivalent of succinic acid will be half the molecular weight ; i.e. $\frac{118}{2}$, or 59.

In the actual determination, aliquot portions of the succinic acid solution are titrated with decinormal baryta solution, using phenolphthalein as the indicator.

For example, in an experiment, 50 c.c. of a solution containing succinic acid required, as a mean of three titrations, 18·6 c.c. of 0·1N.$Ba(OH)_2$ solution to effect the colour change with phenolphthalein.

Then, the normality of the acid solution will be $0.1N. \times \dfrac{18.6}{50}$;

i.e. $5.9 \times \dfrac{18.6}{50}$, or *2.19 grams, of succinic acid per litre.*

N.B.—*By taking an accurately known weight of pure succinic acid crystals and dissolving them in the required volume of water an accurate decinormal solution of the acid may be prepared. This solution can then be used for standardizing the baryta solution, which is liable to vary in strength when kept.*

The Estimation of Citric Acid. Citric acid, which crystallizes with one molecule of water of crystallization, reacts with caustic soda as a tribasic acid. The complete neutralization is indicated when phenolphthalein is the indicator; but if methyl orange be employed, ' equivalence ' is indicated when only *one* of the three replaceable hydrogen atoms has been replaced by sodium. (See § 146.)

The complete reaction takes place according to the equation:

$$\begin{array}{l} CH_2COOH \\ | \\ CH(OH)COOH.H_2O + 3NaOH = \\ | \\ CH_2COOH \end{array} \quad \begin{array}{l} CH_2COONa \\ | \\ CH(OH)COONa + 4H_2O. \\ | \\ CH_2COONa \end{array}$$
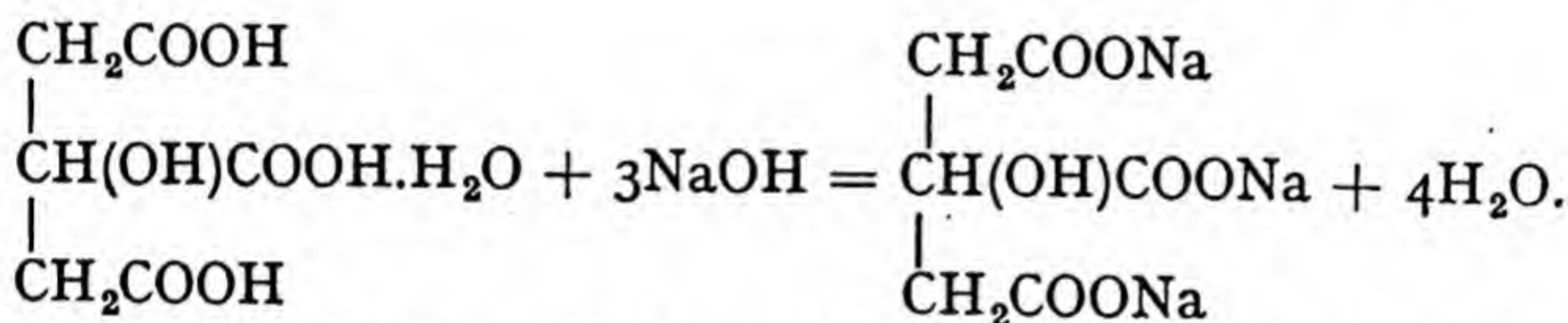
In the actual determination, the solution containing citric acid is titrated with decinormal baryta solution, using phenolphthalein as the indicator. It will be seen from the above equation that the chemical equivalent of citric acid is one-third the molecular weight; i.e. $\dfrac{211}{3}$, or 70.33, in the case of hydrated citric acid; or if anhydrous citric acid be required the equivalent will be $\dfrac{193}{3}$, or 64.33.

For example, suppose that 50 c.c. of a citric acid solution required, as a mean of three titrations, 27.5 c.c. of $0.1N.Ba(OH)_2$ to give the colour change with phenolphthalein:

Then the normality of the acid solution is $0.1N. \times \dfrac{27.5}{50}$, or the strength of the solution is $7.033 \times \dfrac{27.5}{50}$, or *3.88 grams, of hydrated citric acid per litre.*

31. THE DETERMINATION OF THE HARDNESS OF WATER (HEHNER'S METHOD). Hehner has divised a very simple

method for determining the hardness of water by direct titration with $\frac{N}{50}$.H_2SO_4 solution. The best indicator to use is phenacetolin, which is pink in solutions of alkaline carbonates and yellow in acid solution. Methyl orange may be used if phenacetolin is not obtainable.

(a) *Temporary Hardness* is due to the insoluble carbonates of calcium and magnesium being held in solution as bicarbonates by the carbon dioxide dissolved in the water, and they may be precipitated again by boiling the solution ; e.g. :

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$
(insoluble)   (soluble)
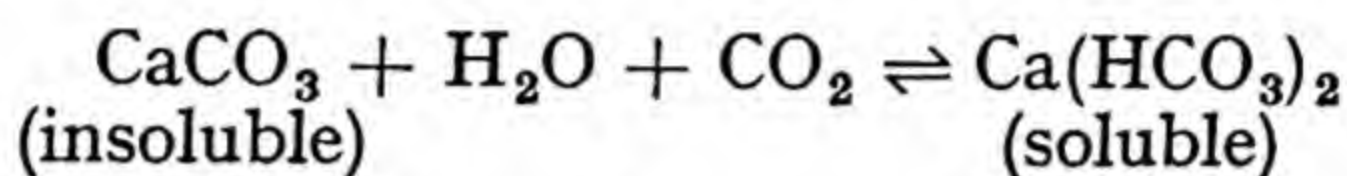
In considering the reaction

$$\underset{100}{CaCO_3} + \underset{98}{H_2SO_4} = CaSO_4 + H_2O + CO_2,$$
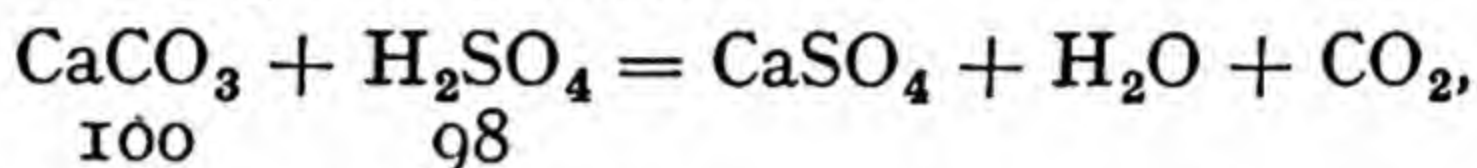
it will be seen that 2 litres of normal sulphuric acid (i.e. 98 grams of H_2SO_4) exactly decompose 100 grams of $CaCO_3$.

Therefore, 1 litre of $\frac{N}{50}$.H_2SO_4 will decompose exactly one gram of $CaCO_3$; i.e. 1 c.c. of $\frac{N}{50}$.H_2SO_4 will be equivalent to 1 milligram of $CaCO_3$.

As the hardness of water is generally expressed directly in grains per gallon (i.e. parts per 70,000), it is best to titrate 70 c.c. of the water at a time, and the water should be heated to boiling. The number of c.c. of $\frac{N}{50}$.H_2SO_4 required to effect the colour change with phenacetolin will, thus, represent the number of milligrams of $CaCO_3$ in 70,000 milligrams of water. The result is thus expressed directly in grains per gallon.

For example, suppose that, as a mean of three titrations, 16·4 c.c. of $\frac{N}{50}$.H_2SO_4 were required to effect the colour change with 70 c.c. of water containing a few drops of phenacetolin :

Then the water contains 16·4 parts of $CaCO_3$ per 70,000 parts of water.

Thus, the *Temporary Hardness* of the water is *16·4* grains of $CaCO_3$ (including the equivalent amount of $MgCO_3$) per gallon.

(b) *Permanent Hardness.* This is due to the sulphates of calcium and magnesium, and it can be determined by precipitating the sulphates as carbonates by means of $\frac{N}{50}$.Na_2CO_3 solution :

$$CaSO_4 \rightleftharpoons \overset{++}{Ca} + \overset{=}{SO_4}$$

$$Na_2CO_3 \rightleftharpoons \overset{=}{CO_3} + \overset{+}{Na} + \overset{+}{Na}$$

$$\downarrow$$

$$CaCO_3$$
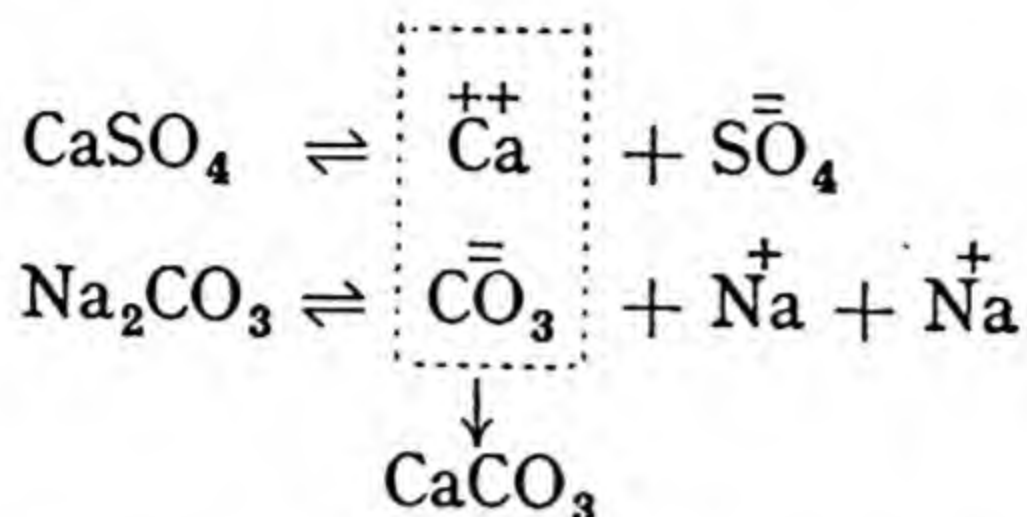
Although the calcium sulphate is so very slightly soluble, the ions, formed by the small amount which is dissolved, are sufficient to cause the complete precipitation of the calcium as carbonate.

Here, 1 c.c. of $\frac{N}{50}$.Na_2CO_3, being equivalent to 1 c.c. of $\frac{N}{50}$.H_2SO_4 will therefore precipitate 1 milligram of $CaCO_3$ (or its equivalent in $MgCO_3$).

In the determination of permanent hardness, 70 c.c. of water are taken, as before, and a measured excess of the $\frac{N}{50}$.Na_2CO_3 solution added. The solution is then evaporated to dryness in a platinum dish on a water bath ; the soluble portion of the residue is extracted with distilled water, filtered, and the filtrate titrated with $\frac{N}{50}$.H_2SO_4, using phenacetolin as the indicator. The titration represents the excess $\frac{N}{50}$.Na_2CO_3 added to the solution, and the difference between this volume and the original volume of Na_2CO_3 represents the volume of $\frac{N}{50}$.Na_2CO_3 used in precipitating the permanent hardness.

For example, suppose that 50 c.c. of $\frac{N}{50}$.Na_2CO_3 were added to the 70 c.c. of water, and that, after evaporation, filtration, etc., 42·7 c.c. of $\frac{N}{50}$.H_2SO_4 were required to neutralize the excess sodium carbonate.

Then, $(50 - 42 \cdot 7)$, or $7 \cdot 3$ c.c. of $\dfrac{N}{50}.Na_2CO_3$, have been used in removing the permanent hardness.

Therefore, the permanent hardness is equivalent to $7 \cdot 3$ grains of $CaCO_3$ (or the equivalent in $MgCO_3$) per gallon.

Thus, the *Permanent Hardness* is *7·3* grains per gallon.

In this case, therefore, the *Total Hardness* of the water is $(16 \cdot 4 + 7 \cdot 3)$, or *23·7* grains per gallon.

N.B.—In the case of a water which contains sodium or potassium carbonates there will be no *true* permanent hardness, since the alkaline carbonates will have decomposed the calcium and magnesium sulphates. The temporary hardness as determined by titration with the $\dfrac{N}{50}.H_2SO_4$ will be greater than the real value, and will represent the total hardness. The true temporary hardness can be estimated by proceeding in exactly the same way as in the determination of permanent hardness. In this case, on titrating the sodium carbonate with the H_2SO_4 it will be found that the amount of Na_2CO_3 is in excess of the amount added. The difference between these amounts is the amount of alkaline carbonate present in the original water, and the *true* temporary hardness is obtained by subtracting this amount from the apparent temporary hardness.

32. THE PREPARATION OF STANDARD SOLUTIONS OF ACIDS. The table on p. 45 gives the specific gravities and percentage compositions of the three common mineral acids, and will be found of great value in preparing approximately standard solutions of those acids.

SUGGESTED EXPERIMENTS ON CHAPTER II

1. You are provided with pure, anhydrous sodium bicarbonate. Prepare an accurately decinormal solution of sodium carbonate, and, by means of this solution, standardize a solution of sulphuric acid.

2. Given a normal solution of HCl, estimate the strength, in grams per c.c., of the bench NaOH solution. Take 25 c.c. of the NaOH solution and dilute it to 250 c.c. Use this solution for your determination.

3. You are provided with accurately decinormal nitric acid, and approximately decinormal caustic potash solution. Determine the strength of the bench sulphuric acid in grams per c.c.

4. Given an accurately decinormal solution of sulphuric acid, find the percentage of NaOH in commercial caustic soda.

5. Determine the strength of the given solution of potassium

SPECIFIC GRAVITIES AND PERCENTAGE COMPOSITIONS OF THREE
COMMON MINERAL ACIDS

Hydrochloric Acid		Nitric Acid		Sulphuric Acid	
S.G.	Per cent. HCl	S.G.	Per cent. HNO$_3$	S.G.	Per cent. H$_2$SO$_4$
1·212	42·9	1·530	99·84	1·842	100
1·210	42·4	1·529	99·52	1·796	86·5
1·205	41·2	1·514	95·27	1·753	81·7
1·199	39·8	1·506	93·01	1·711	78·1
1·195	39·0	1·494	89·58	1·672	74·7
1·190	37·9	1·486	87·45	1·634	71·6
1·185	36·8	1·482	86·17	1·597	68·6
1·180	35·7	1·463	80·96	1·563	65·5
1·175	34·7	1·438	74·01	1·530	62·5
1·171	33·9	1·432	72·39	1·498	59·6
1·166	33·0	1·429	71·24	1·468	56·9
1·161	32·0	1·419	69·20	1·438	54·0
1·157	31·2	1·400	65·07	1·410	51·2
1·152	30·2	1·381	61·21	1·383	48·3
1·143	28·4	1·372	59·59	1·357	45·5
1·134	26·6	1·353	56·10	1·332	43·0
1·125	24·8	1·331	52·33	1·308	40·2
1·116	23·1	1·323	50·99	1·285	37·4
1·108	21·5	1·298	47·18	1·263	34·7
1·100	19·9	1·274	43·53	1·241	32·2
1·091	18·1	1·237	37·95	1·220	29·6
1·083	16·5	1·211	33·86	1·200	27·1
1·075	15·0	1·172	28·00	1·180	24·5
1·067	13·4	1·157	25·71	1·162	22·2
1·060	12·0	1·105	17·47	1·142	19·6
1·052	10·4	1·067	11·41	1·125	17·3
1·044	8·9	1·045	7·72	1·108	15·2
1·036	7·3	—	—	1·091	13·0
1·029	5·8	—	—	1·075	10·8
1·022	4·5	—	—	1·060	8·8
1·014	2·9	—	—	1·045	6·8

hydrogen oxalate in grams per litre. Potassium hydrogen oxalate acts as a monobasic acid. What indicator will you use, and why ?

6. By means of normal caustic soda solution determine the strength of the given solutions of (a) potassium hydrogen sulphate, and (b) potassium bicarbonate. What indicator will you use in each case ? Give reasons for your choice.

7. You are provided with decinormal sulphuric acid, and are asked to determine the percentage composition of the given mixture of potassium carbonate and potassium bicarbonate.

8. Given a decinormal solution of KOH, find the respective amounts of HCl and H_2SO_4 in 1 litre of the given solution.

N.B.—The total amount of acid must be known.

9. You are provided with decinormal HCl and are asked to determine the strength of the bench ammonia solution in grams per litre. What indicator will you use, and why ?

10. You are provided with decinormal solutions of KOH and Na_2CO_3, and are asked to determine the strength, in grams per litre, of the given solution of acetic acid. Which of the two standard solutions will you employ, and what indicator will you use ? Give reasons for your choice.

11. You are provided with an accurately decinormal solution of oxalic acid and an accurately decinormal solution of nitric acid. You are required to determine the strength, in grams per c.c., of the given sodium carbonate solution. Which standard acid solution will you employ, and what indicator will you use ? Give reasons for your choice.

12. You are provided with one-fifth normal solutions of sodium carbonate and hydrochloric acid, and are required to determine the percentage purity of the given barium chloride, $BaCl_2.2H_2O$.

13. Given normal solutions of HCl and NaOH, find the equivalent weight of tin.

N.B.—Use pure tinfoil.

14. You are provided with an accurately decinormal solution of HCl and an approximately decinormal solution of KOH. Find the equivalent weight of H_2SO_4 given a 1 per cent solution of sulphuric acid.

15. You are provided with normal solutions of caustic soda and sulphuric acid. Determine the percentage of ammonia in (a) ammonium nitrate, and (b) ammonium chloride.

16. Given normal solutions of NaOH and HCl find the equivalent weight of pure magnesium oxide.

17. You are provided with normal solutions of HCl and KOH. Find the percentage of $CaCO_3$ in the given sample of chalk, assuming that the only impurity present in the chalk is calcium sulphate.

18. You are provided with decinormal solutions of sulphuric acid and sodium carbonate, and you are required to determine the number of molecules of water of crystallization in hydrated copper sulphate.

19. You are provided with pure, hydrated borax and decinormal HCl. Determine the percentage of water of crystallization in the hydrated borax.

20. You are provided with decinormal KOH, methyl orange, and a sample of phosphorus pentoxide. You are required to determine the percentage purity of the oxide.

Take an accurately known weight of the phosphorus pentoxide, boil with a suitable amount of distilled water for about half an hour (taking care to avoid loss by spitting), cool, and dilute to a convenient volume.

If necessary, the solution must be filtered before dilution. Use this solution for the determination.

21. Prepare equal volumes (say 200 c.c.) of the following :

10, 20, 30, 50, 75, and 100 per cent (by volume) concentrated sulphuric acid.

You are provided with pure zinc-foil and normal NaOH, and are required to plot a curve showing the rate of evolution of hydrogen in the reaction

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

with varying concentrations of sulphuric acid.

Take the same weight of zinc-foil in each experiment, and withdraw 10 c.c. of the reacting solution every three minutes ; dilute each portion to suitable volume (calculate the required volume approximately) and titrate with the normal NaOH. The amount of acid changed in each case will give an indication of the rate of the reaction.

CHAPTER III

VOLUMETRIC ESTIMATIONS BASED UPON OXIDATION AND REDUCTION METHODS (Part 1)

POTASSIUM PERMANGANATE

33. Potassium permanganate, $KMnO_4$, reacts in acid solution as an oxidizing agent. Actually, two molecules of $KMnO_4$ liberate five atoms of oxygen, which are thus available for oxidizing purposes ; e.g.

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$
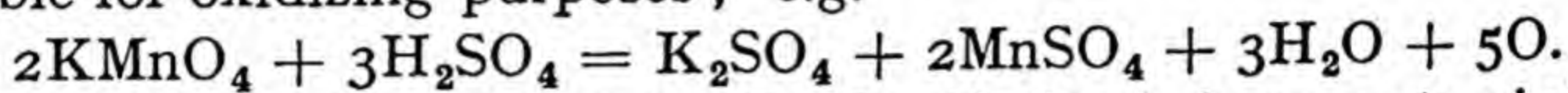
The $KMnO_4$ is reduced to K_2SO_4 (derived from potassium oxide, K_2O), and manganous sulphate $MnSO_4$ (derived from manganous oxide, MnO).

If, therefore, we write $2KMnO_4$ as $K_2Mn_2O_8$, we may represent this compound as being composed of the two oxides : potassium oxide, K_2O, and manganese heptoxide, Mn_2O_7.

Thus, $$K_2Mn_2O_8 \equiv K_2O + Mn_2O_7.$$
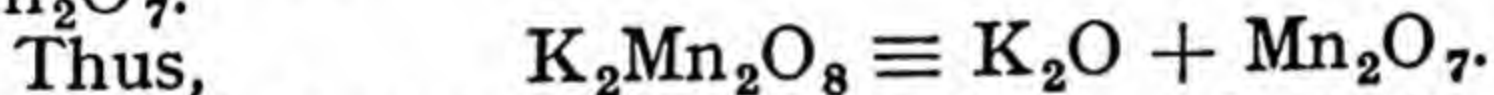
We may, therefore (since $MnSO_4$ is the salt corresponding to the basic oxide MnO), represent the reduction of two molecules of potassium permanganate by the equation :

$$Mn_2O_7 \rightarrow 2MnO + 5O.$$

Thus, $$2KMnO_4 \equiv 5O \equiv 10H.$$
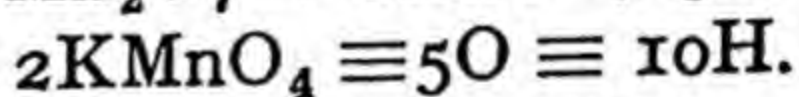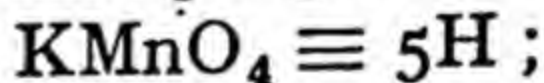
Therefore $$KMnO_4 \equiv 5H ;$$

i.e. the chemical equivalent of $KMnO_4$, when used as an oxidizing agent in acid solution, is *one-fifth* the molecular weight.

Thus, a normal solution of $KMnO_4$ contains $\frac{158}{5}$, or 3·16 grams, of pure $KMnO_4$ per litre.

It will, therefore, be appreciated that a normal solution of $KMnO_4$ is, in effect, a normal ' available oxygen ' solution, since 1 litre of the $N.KMnO_4$ solution will liberate 8 grams of oxygen available for oxidation purposes.

In practice, it is customary to employ decinormal solutions of $KMnO_4$, as this strength is quite strong enough for most oxidation operations.

34. PRECAUTIONS NECESSARY WHEN TITRATING WITH
POTASSIUM PERMANGANATE. (1) Dilute sulphuric acid must
always be present in sufficient excess to prevent the pre-
cipitation of hydrated oxide of manganese. If a brown
precipitate or any turbidity is observed more sulphuric acid
must be added at once.

(2) Always titrate slowly when using permanganate, for
the same reason.

(3) Hydrochloric and nitric acids should not be employed
to acidify the solution, since the reaction may be complicated
by the liberation of chlorine from HCl, and of oxides of
nitrogen from nitric acid.

(4) When titrating oxalic acid, or a solution of an oxalate,
the solution should be warmed to about 60° C., otherwise the
'end-point' of the reaction is indistinct.

x (5) The permanganate solution should always be placed
in a burette fitted with a glass stopcock, as rubber tubing is
attacked by the permanganate, and the titration is conse-
quently inaccurate.

x(6) All the distilled water used for making solutions of
ferrous salts, etc., should be freshly boiled, so as to eliminate
dissolved atmospheric oxygen which might oxidize some of
the ferrous salt to the ferric state.

(7) Potassium permanganate must not be used to estimate
chlorides of iron. Potassium dichromate must be used instead.

35. THE OXIDATION OF FERROUS SALTS BY POTASSIUM
PERMANGANATE. Ferrous salts are oxidized to the ferric
state by $KMnO_4$ solution in the presence of sulphuric acid.
Thus, ferrous sulphate is oxidized to ferric sulphate according
to the equation :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$
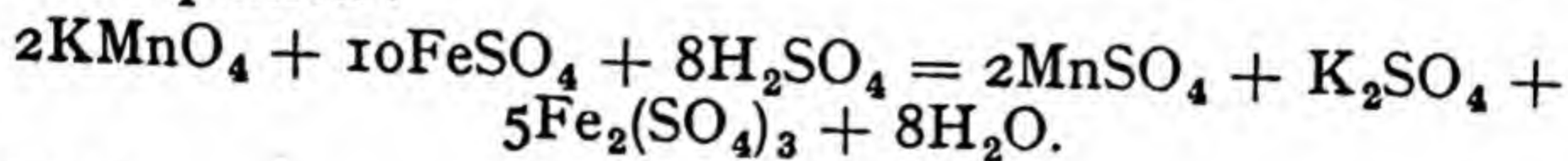
Here,
$$2KMnO_4 \equiv 10Fe$$
$$316 \qquad 10 \times 56$$

Therefore 1 litre of 0·1N.$KMnO_4$ (3·16 grams) will oxidize
exactly 5·6 grams of iron from the ferrous to the ferric state.

A decinormal solution of $KMnO_4$ can be prepared by weigh-
ing accurately 3·16 grams of the purest recrystallized salt,
dissolving in distilled water, and then making up to 1 litre
with more distilled water in a graduated flask. If, however,
the ordinary 'pure' $KMnO_4$ is employed, about 3·5 grams of
the salt should be taken and the solution standardized in one
of the following ways :

4

THE STANDARDIZATION OF POTASSIUM PERMANGANATE

(a) Potassium permanganate can be standardized with reference to metallic iron. The usual method consists of taking a convenient weight of the purest, softest iron wire (containing about 99·6% Fe), dissolving it in air-free dilute sulphuric acid, and making up this solution to a suitable volume with freshly boiled distilled water. The iron solution is then titrated with the approximately o·1N.KMnO$_4$ solution, and the permanganate is then determined from the equivalents:

$$2KMnO_4 \equiv 10Fe.$$
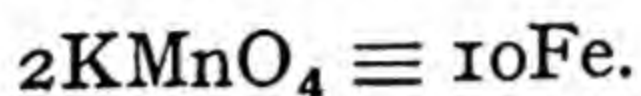
This method, however, is open to objection. In the first place, the purity of the iron wire is not accurately known; secondly, despite the precautions taken to prevent the oxidation of the ferrous sulphate to the ferric state, it is doubtful whether all the iron remains in the ferrous condition. A more accurate method based on the equivalent of iron is to use ferrous ammonium sulphate, which is not easily oxidized by atmospheric oxygen.

The Standardization of KMnO$_4$ by Means of Ferrous Ammonium Sulphate. Ferrous ammonium sulphate, FeSO$_4$.(NH$_4$)$_2$.SO$_4$.6H$_2$O, can easily be obtained in a state of purity by preparing it in the crystalline form by dissolving equivalent amounts of ferrous sulphate and ammonium sulphate in distilled water, gently evaporating the solution to saturation point, and cooling slowly. The crystals thus obtained can then be recrystallized and dried.

The formula weight of ferrous ammonium sulphate (392 grams) contains exactly one-seventh of its weight of iron (56 grams). It is thus quite easy to make up a standard iron solution from this salt.

Method. A known weight of the pure recrystallized salt is dissolved and made up to a convenient volume with freshly boiled distilled water in a graduated flask; 25 c.c. of this solution are then transferred to a small flask, about 15 c.c. of dilute sulphuric acid are added, and the approximately decinormal permanganate is run in slowly from the burette until a faint pink colour is imparted to the solution (see the precautions in § 34). Three concordant results are obtained and the potassium permanganate is then standardized.

Suppose that 9·87 grams of pure recrystallized ferrous ammonium sulphate were dissolved in air-free distilled water

and made up to 250 c.c., and that, as a mean of three titrations, 23·5 c.c. of the approximately decinormal permanganate were required to completely oxidize 25 c.c. of the ferrous solution.

Then 250 c.c. of the iron solution contain $\dfrac{9·87}{7}$, or 1·41 grams, of Fe.

Therefore 25 c.c. of the solution contain 0·141 gram of Fe.

And, since 56 grams of iron are equivalent to 31·6 grams of $KMnO_4$, 0·141 grams of Fe will be equivalent to $\dfrac{31·6}{56} \times 0·141$ grams of $KMnO_4$. The strength of the $KMnO_4$ solution is, therefore,

$$\frac{1000}{23·5} \times \frac{31·6}{56} \times 0·141,\ \textit{or 3·39 grams per litre.}$$

Thus the normality of the $KMnO_4$ solution is $\dfrac{3·39}{3·16} \times \dfrac{N}{10}$.

The volume of water required to dilute 1 litre of the permanganate solution to accurately decinormal strength can then be calculated :

3·16 grams of $KMnO_4$ are contained in 1000 c.c. of 0·1N. solution.

3·39 grams of $KMnO_4$ are contained in $1000 \times \dfrac{3·39}{3·16}$, or 1072 c.c., of 0·1N. solution.

Thus (1072 — 1000), or 72 c.c., of water must be added to 1 litre of the potassium permanganate solution in order to make it accurately decinormal.

(b) *The Standardization of $KMnO_4$ by means of Oxalic Acid.* Oxalic acid, $(COOH)_2.2H_2O$, is easily oxidized by potassium permanganate solution to carbon dioxide and water in the presence of dilute sulphuric acid. The reaction proceeds best at a temperature of about 60° C., and may be represented by the equation :

$$5(COOH)_2.2H_2O + 2KMnO_4 + 3H_2SO_4 = 10CO_2 +$$
$$K_2SO_4 + 2MnSO_4 + 10H_2O.$$
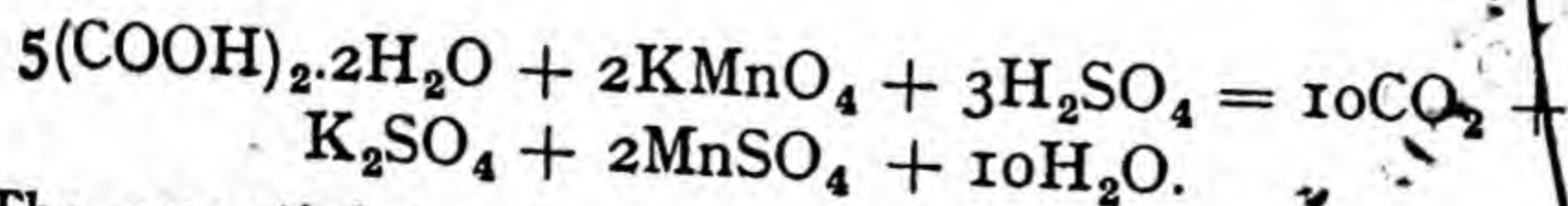
The essential reaction can be represented

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + O = 2CO_2 + H_2O.$$
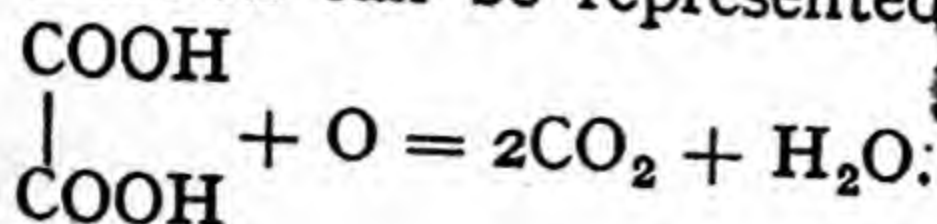
Thus, one molecule of the acid is equivalent to one atom of oxygen, and, therefore, to two atoms of hydrogen.

Therefore, the chemical equivalent of oxalic acid will be half the molecular weight ; i.e. $\frac{126}{2}$, or 63·0, in the case of the hydrated acid, $(COOH)_2.2H_2O$; and $\frac{90}{2}$, or 45·0, in the case of the anhydrous acid, $(COOH)_2$.

A normal solution is, therefore, a semi-molar solution, and will contain 63·0 grams of the hydrated oxalic acid per litre.

Method. A suitable amount of the hydrated acid is weighed accurately, dissolved, and made up to a convenient volume with distilled water. 25 c.c. of this solution are transferred to a small flask, an equal volume of dilute sulphuric acid is added, and the solution heated until the temperature is about 60° C. The permanganate is then run very slowly into the flask until a faint colour persists (see § 34). Three concordant results are obtained and the permanganate is then standardized.

Suppose that, in an experiment, 24·8 c.c. of the approximately decinormal $KMnO_4$ were required to neutralize 25 c.c. of an oxalic acid solution containing 1·59 grams of $(COOH)_2.2H_2O$ per 250 c.c. :

Therefore 25 c.c. of the acid solution contains 0·159 grams of $(COOH)_2.2H_2O$; and this amount is equivalent to

$$0\cdot159 \times \frac{31\cdot6}{63\cdot0} \text{ grams of } KMnO_4.$$

Therefore the strength of the $KMnO_4$ solution is :

$$0\cdot159 \times \frac{31\cdot6}{63} \times \frac{1000}{24\cdot8}, \text{ or } 3\cdot22 \text{ grams, } per \text{ } litre.$$

Thus, the normality of the $KMnO_4$ solution is $\frac{3\cdot22}{3\cdot16} \times N.$, and, since 3·22 grams of $KMnO_4$ will be contained in 1000 $\times$ $\frac{3\cdot22}{3\cdot16}$, or 1019 c.c., of decinormal $KMnO_4$ solution, it follows that (1019–1000), or *19 c.c.*, of water must be added to 1 litre of the $KMnO_4$ solution to make it accurately decinormal.

The strength of any oxalic acid solution may be determined in a similar manner by titrating the acid solution with decinormal $KMnO_4$, and calculating the weight of oxalic acid which has reacted with the observed volume of standard permanganate.

DETERMINATIONS WITH STANDARD POTASSIUM PERMANGANATE

36. THE ESTIMATION OF FERROUS SALTS. The estimation of ferrous salts, with the exception of the chlorides, is carried out in a similar manner to the standardization of potassium permanganate with ferrous ammonium sulphate.

A known weight of the ferrous salt is dissolved in freshly boiled distilled water and diluted to a convenient volume. Aliquot portions of this solution are acidified with dilute sulphuric acid, and titrated with $0 \cdot 1N.KMnO_4$ solution, 1 c.c. of which is equivalent to 0·0056 gram of Fe.

For example, in determining the percentage of iron in ferrous ammonium sulphate, 9·604 grams of the pure recrystallized salt were dissolved in air-free distilled water and made up to 250 c.c.

As a mean of three titrations, 25 c.c. of this solution (acidified with dilute sulphuric acid) required 24·5 c.c. of $0 \cdot 1N.KMnO_4$ for complete oxidation to the ferric state.

Now, since 1 c.c. of $0 \cdot 1N.KMnO_4$ is equivalent to 0·0056 gram of Fe, it follows that 24·5 c.c. of $0 \cdot 1N.KMnO_4$ are equivalent to 0·0056 × 24·5, or *0·137 gram, of Fe.*

Therefore, 250 c.c. of the ferrous salt contain 1·37 grams of Fe.

Thus, the percentage of iron in ferrous ammonium sulphate is

$$\frac{1 \cdot 37}{9 \cdot 604} \times 100, \text{ or } 14 \cdot 3\%.$$

37. THE DETERMINATION OF FERRIC SALTS. Ferric salts, with the exception of the chlorides, are determined by reduction to the ferrous state and the estimation of the ferrous iron in the ordinary way. There are three common ways in which the reduction of the ferric salt to the ferrous state may be performed.

(1) *Reduction by Means of Zinc and Dilute Sulphuric Acid.* A large excess of zinc (which must be free from iron, arsenic, and similar impurities) is added, together with dilute sulphuric acid, to the solution of ferric salt.

The hydrogen evolved in the reaction of the metal and the sulphuric acid reduces the ferric salt to the ferrous state, and the reaction, in the case of ferric sulphate, may be represented thus :

$$Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4.$$
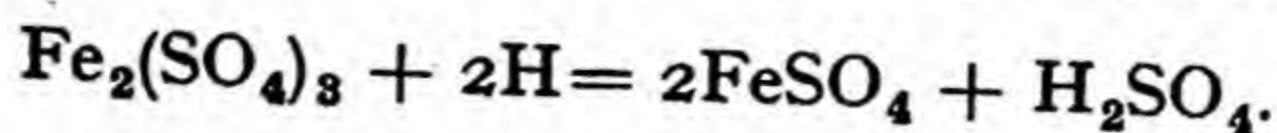
It can be ascertained when reduction is complete by withdrawing a drop of the solution on the end of a glass rod and bringing it into contact with a drop of ammonium thiocyanate solution upon a white tile. This test is based upon the fact that, with ferric salts, ammonium thiocyanate, NH_4CNS, gives a blood-red coloration of ferric thiocyanate, $Fe(CNS)_3$, whereas with ferrous salts there is no colour change. Thus, any remaining ferric salt will be indicated by the red colour, and the reduction is continued until the red colour is no longer observed. The excess metal is then separated from the solution by decantation, or, if necessary, by filtration. The solution is then allowed to cool, diluted to a convenient volume, and aliquot portions are titrated with decinormal permanganate in the presence of sulphuric acid (as a rule, the acid added to liberate hydrogen from the zinc is sufficient, but, if the slightest turbidity be observed during the titration, more sulphuric acid must be added).

(2) *Reduction by Means of Sulphur Dioxide.* In this method of reducing the ferric salt to the ferric state only * dilute solutio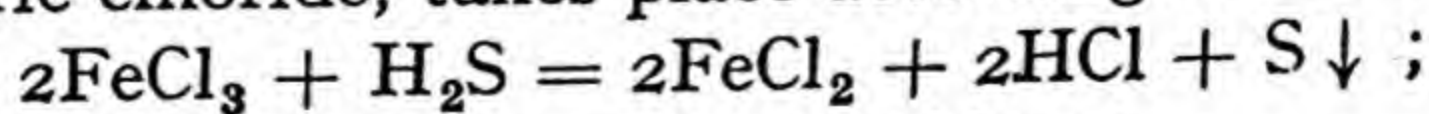ns should be employed. Sulphur dioxide, either from a siphon or prepared by the action of dilute sulphuric acid on sodium sulphite, is bubbled through the dilute ferric iron solution, which is heated to boiling. The action is continued until no remaining ferric iron can be detected by the NH_4CNS test; the solution is then boiled until all the sulphur dioxide has been expelled, cooled, diluted to suitable volume, and aliquot portions are titrated with decinormal permanganate in the presence of dilute sulphuric acid.

The reaction, in the case of ferric sulphate, is represented by the equation :

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4.$$
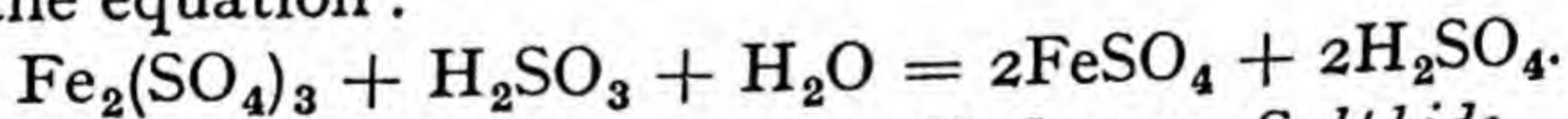
(3) *Reduction by Means of Hydrogen Sulphide.* Here, again, dilute solutions only should be used. It is best to divide the ferric iron solution into aliquot portions at the start, and repeat the reduction with each portion. The ferric iron solution is acidified with dilute sulphuric acid and then saturated with hydrogen sulphide gas. The reaction, in the case of ferric chloride, takes place according to the equation :

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S\downarrow \;;$$

or, expressing the reaction in terms of ions :

$$2\overset{+++}{Fe} + 6\overset{-}{Cl} + \overset{+}{H} + \overset{-}{HS} \rightarrow 2\overset{++}{Fe} + 4\overset{-}{Cl} + 2\overset{+}{H} + 2\overset{-}{Cl} + S\downarrow.$$
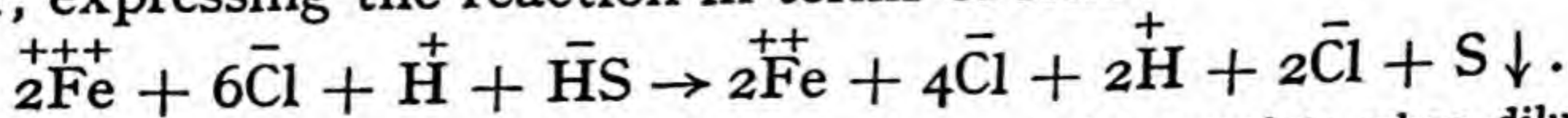
* This is most important as the reduction is only complete when dilute solutions of ferric salts are employed.

The essential reaction is, thus, between the ferric and the hydrosulphide ions :

$$2\overset{+++}{Fe} + \overset{-}{HS} \rightarrow 2\overset{++}{Fe} + \overset{+}{H} + S \downarrow .$$
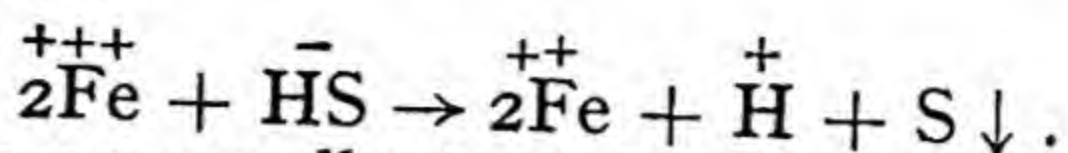
This reaction is an excellent example of reduction which is essentially a change involving the loss of a positive charge.

The reduction is continued until the NH_4CNS test indicates that all the ferric salt has been converted to the ferrous state. The excess H_2S dissolved in the solution is boiled off (the completion of the operation can be ascertained with lead acetate paper) ; the precipitated sulphur is filtered off and washed well with distilled water, and the combined filtrate and washings are titrated with $0.1N.KMnO_4$ solution in the presence of dilute sulphuric acid.

TO FIND THE PERCENTAGE OF IRON IN A FERRIC SALT

An accurately known weight of the ferric salt is dissolved in water, diluted to a suitable volume, and reduced to the ferrous state by one of the methods described above. The NH_4CNS test is applied until the reduction is complete ; the solution is then cooled and diluted to convenient volume in a graduated flask.

For example, in an experiment, 9.37 grams of a ferric salt were dissolved in air-free distilled water, reduced, and the reduced iron solution made up to 500 c.c. As a mean of three titrations, 50 c.c. of this solution required 19.4 c.c. of $0.1N.KMnO_4$ solution for complete oxidation to the ferric state.

Therefore, 194 c.c. of $0.1N.KMnO_4$ would be required to oxidize the whole 500 c.c. of the reduced iron solution.

And 194 c.c. of $0.1N.KMnO_4$ are equivalent to 194×0.0056 grams of Fe.

Therefore, the percentage of iron in the ferric salt is

$$\frac{194 \times 0.0056}{9.37} \times 100 ; \text{ i.e. } \textit{11.6\% Fe.}$$

38. THE ESTIMATION OF A MIXTURE OF FERROUS AND FERRIC SALTS. Solutions which contain a mixture of ferrous and ferric salts may be estimated by a combination of the two methods just described separately. The *Ferrous* iron is first determined directly by titrating aliquot portions of the mixture with decinormal permanganate. Another portion of the mixture is then reduced by one of the standard

methods (see § 37), and is diluted to a suitable volume. Aliquot portions of this solution are then titrated with $0.1N.KMnO_4$, and the result will give the *Total* iron in the solution. The *Ferric* iron is then obtained by difference.

For example, in an experiment, 20 c.c. of the iron solution required 14·7 c.c. of $0.1N.KMnO_4$ for oxidation of the ferrous iron to the ferric state. 50 c.c. of the solution were then reduced with sulphur dioxide, and the solution made up to 200 c.c. with distilled water ; 50 c.c. of this reduced solution were then titrated with $0.1N.KMnO_4$, and, as a mean of three titrations, 13·6 c.c. were required.

The calculation is in three steps.

(a) *The Estimation of the Ferrous Iron.* 14·7 c.c. of $0.1N.KMnO_4$ are equivalent to 14·7 × 0·0056 grams of Fe. Therefore, the amount of ferrous iron in 1 litre of the solution is

$$14·7 \times 0·0056 \times \frac{1000}{20}, \text{ or } 4·12 \text{ grams, of } ferrous\ iron.$$

(b) *The Estimation of the Total Iron.* 50 c.c. of the reduced and diluted iron solution are equivalent to 13·6 c.c. of $0.1N.KMnO_4$.

Therefore, 200 c.c. (i.e. 50 c.c. of the original solution) are equivalent to 13·6 × 4, or 54·4 c.c. of $0.1N.KMnO_4$.

And 54·4 c.c. of $0.1N.KMnO_4$ are equivalent to 54·4 × 0·0056 grams of Fe.

Therefore, the amount of total iron in 1 litre of the mixture is

$$54·4 \times 0·0056 \times \frac{1000}{50}, \text{ or } 6·09 \text{ grams, of } total\ iron.$$

(c) *The Estimation of the Ferric Iron.* In consequence, the amount of ferric iron in 1 litre of the mixture is (6·09−4·12), or *1·97* gram, of *ferric iron*.

Thus, the solution contains *4·12* grams of *ferrous iron* and *1·97* grams of *ferric iron* per litre.

39. To DETERMINE THE PERCENTAGE OF WATER OF CRYSTALLIZATION IN HYDRATED POTASSIUM OXALATE. About 2·5 grams of the oxalate are dissolved in distilled water and diluted to 250 c.c. Aliquot portions of this solution are acidified with excess of dilute sulphuric acid, and titrated with $0.1N.KMnO_4$ at a temperature of about 60° C., exactly as in the case of oxalic acid.

For example, in an experiment, 2·415 grams of the pure crystalline oxalate were made up to 250 c.c. (i.e. 9·66 grams per litre). As a mean of three titrations, 25 c.c. of this

solution required 25·2 c.c. of o·1NKMnO$_4$ for complete oxidation.

Now, $2KMnO_4 \equiv 5(COOH)_2 \equiv 5(COOK)_2$
anhydrous

Therefore, 316 grams of KMnO$_4$ $\equiv$ 830 grams of (COOK)$_2$;

i.e. 1 litre of o·1N.KMnO$_4$ $\equiv$ 8·3 grams of (COOK)$_2$;

∴ 25·2 c.c. of o·1N.KMnO$_4$ $\equiv$ 25·2 × 0·0083 of (COOK)$_2$.

Therefore, the weight of anhydrous potassium oxalate in 1 litre of the solution is

$$25·2 \times 0·0083 \times \frac{1000}{25}, \text{ or } 8·36 \text{ grams, of (COOK)}_2.$$

Now,

$$\frac{\text{Molecular weight of hydrated potassium oxalate}}{\text{Molecular weight of anhydrous potassium oxalate}} = \frac{9·66}{8·36}.$$

Therefore, $$\frac{M}{116} = \frac{9·66}{8·36};$$

i.e. the molecular weight of hydrated potassium oxalate, M = 134. And the weight of water of crystallization in 134 grams of hydrated potassium oxalate is (134 − 116), or *18* grams.

Therefore, the percentage of water of crystallization in hydrated potassium oxalate is

$$\frac{18}{134} \times 100, \text{ or } 13·4\%.$$

Thus, one molecule of potassium oxalate is associated with $\frac{18}{18}$, or *one* molecule, of water of crystallization.

40. THE ESTIMATION OF HYDROGEN PEROXIDE. Hydrogen peroxide (in aqueous solution) reacts with potassium permanganate, in the presence of sulphuric acid, liberating oxygen. Since *two* molecules of the permanganate are equivalent to *five* atoms of oxygen, it follows that two molecules of permanganate will also be equivalent to five molecules of hydrogen peroxide. The reaction is represented by the equation :

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$
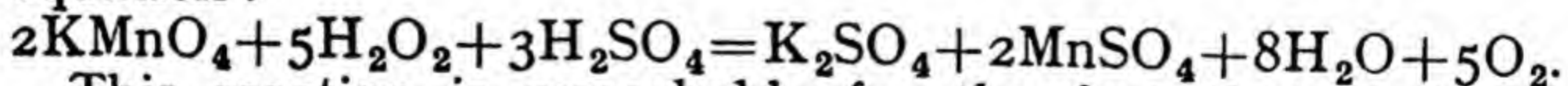
This reaction is remarkable for the fact that both the permanganate and peroxide, which are powerful oxidizing agents, *reduce* one another with the liberation of oxygen.

In estimating the strength of a solution of hydrogen peroxide, aliquot portions of the solution are acidified with dilute sulphuric acid and titrated with standard permanganate solution.

For example, 25·0 c.c. of a hydrogen peroxide solution required, as a mean of three titrations, 23·5 c.c. of o·1N.KMnO$_4$ for complete reduction.

Then, since 2 molecules of permanganate are equivalent to 5 molecules of hydrogen peroxide, it follows that

$$316 \text{ grams of } KMnO_4 \equiv 170 \text{ grams of } H_2O_2.$$

Therefore 1 litre of o·1N.KMnO$_4$ $\equiv$ 1·7 grams of H$_2$O$_2$,

and 23·5 c.c. of o·1N.KMnO$_4$ $\equiv$ 0·0017 $\times$ 23·5 of H$_2$O$_2$.

Thus, the strength of the hydrogen peroxide solution in grams per litre is

$$0·0017 \times 23·5 \times \frac{1000}{25}, \text{ or } 1·59 \text{ grams.}$$

41. THE DETERMINATION OF METALS BY MEANS OF POTASSIUM PERMANGANATE. There are two main methods by which metals may be estimated, using potassium permanganate :

(1) *The Determination of Metals which Form Insoluble Oxalates*, e.g. calcium, barium, strontium ; in fact, nearly all metals, since only sodium, potassium, and ammonium oxalates are readily soluble in water.

(2) *The Determination of Metals which Form Insoluble Sulphides*, e.g. (a), those sulphides which are precipitated from acid solution, viz. mercury, lead, bismuth, copper, cadmium, tin, silver, antimony, platinum, and gold.

(b) Those metals which are not precipitated from acid solution but are precipitated by ammonium sulphide, viz. iron (though this metal would be estimated in the ordinary way as ferrous iron), cobalt, nickel, manganese, zinc, chromium and aluminium.

It will thus be observed that we have a method of estimating almost any metal ; though, of course, in some cases, the method may not be extremely accurate : as, for example, with those metals which form oxalates or sulphides which are slightly soluble. In general, however, almost any metal may be estimated approximately, at least, by one of the above methods. An example based on each of these methods is given in the ensuing paragraphs.

42. THE DETERMINATION OF METALS WHICH FORM INSOLUBLE OXALATES. The method employed is to precipitate the insoluble oxalate by means of ammonium oxalate, and then decompose it with dilute sulphuric acid. The resulting oxalic acid is then estimated in the usual way with

standard potassium permanganate ; e.g. *The Estimation of Calcium in Iceland Spar.* A known weight of the Iceland Spar is placed in a beaker and dissolved in dilute sulphuric acid ; the beaker is covered with a watch-glass during this operation to prevent loss by spitting. A little ammonium chloride and then ammonium hydroxide are added until the solution is alkaline ; the calcium is then completely precipitated by the addition of ammonium oxalate solution. The solution is filtered, and the residue well washed with distilled water to free it from any ammonium oxalate which may be adhering to the precipitate ; the filter paper is then placed in a dish with dilute sulphuric acid and the calcium oxalate is decomposed into oxalic acid and calcium sulphate according to the equivalent :

$$(COO)_2Ca + H_2SO_4 = CaSO_4 + (COOH)_2.$$
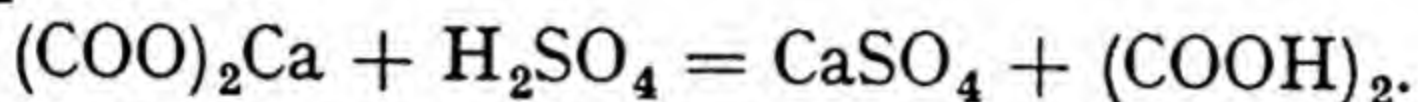
The insoluble calcium sulphate is filtered off, washed with distilled water, and the combined filtrate and washings diluted with distilled water to a suitable volume. Aliquot portions of this solution are then titrated with decinormal potassium permanganate solution at a temperature of about 60° C. The amount of calcium in the solution can then be calculated from the equivalents :

$$2KMnO_4 \equiv 5(COOH)_2 \equiv 5Ca.$$
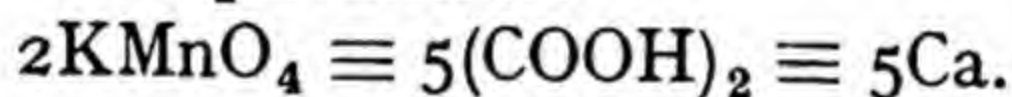
Therefore 31·6 grams of $KMnO_4$ are equivalent to 20 grams of Ca, and 1 litre of 0·1N.$KMnO_4$ will be equivalent to 2·0 grams of Ca.

For example, suppose that 1·43 grams of Iceland Spar were taken, and, after solution in dilute sulphuric acid, precipitation with ammonium oxalate, and decomposition with dilute sulphuric acid, that the solution was diluted to 500 c.c.

Suppose, also, that, as a means of three titrations, 50 c.c. of the diluted solution required 28·6 c.c. of 0·1N.$KMnO_4$ for complete oxidation.

Then, since 1 litre of 0·1N.$KMnO_4$ is equivalent to 2·0 grams of Ca, 28·6 c.c. of 0·1M.$KMnO_4$ will be equivalent to 28·6 × 0·002, or 0·0572 grams of Ca. Therefore, 500 c.c. of the diluted solution will contain 0·572 grams of Ca. Thus the percentage of calcium in Iceland Spar is

$$\frac{0·572}{1·43} \times 100, \text{ or } 40\%.$$

N.B.—This method of determination could also be employed with most metals, excepting sodium and potassium, unless a better special method is in existence.

43. THE ESTIMATION OF METALS WHICH FORM INSOLUBLE SULPHIDES. This method is subdivided into two classes of determinations :

(a) those metals which form sulphides *insoluble in acid solution*, and

(b) those metals which form sulphides *soluble in acids* (see § 41).

(a) *The Determination of Lead in Lead Nitrate as an Example of a Metal which Forms a Sulphide Insoluble in Acid Solution.* A known weight of pure crystalline lead nitrate is diluted to a convenient volume with distilled water ; this solution is then warmed and saturated with dry hydrogen sulphide from a Kipp's apparatus, black lead sulphide being precipitated according to the equation :

$$Pb(NO_3)_2 + H_2S \rightleftharpoons PbS + 2HNO_3.$$

The lead sulphide is separated by filtration. Since the reaction is reversible to some extent, the filtrate is again saturated with hydrogen sulphide and any precipitated lead sulphide filtered off ; this operation must be repeated until no more lead sulphide is precipitated from the filtrate. The collected precipitates are then allowed to react with excess of ferric sulphate solution ; in this way the ferric sulphate is reduced to ferrous sulphate solution according to the equation :

$$PbS + Fe_2(SO_4)_3 = PbSO_4 + 2FeSO_4 + S.$$
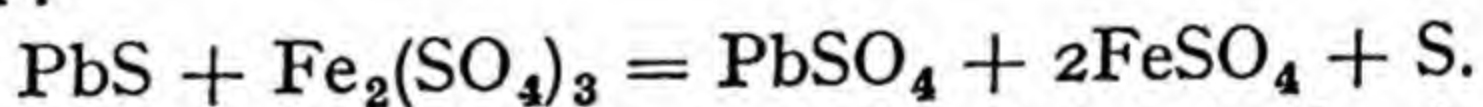
The precipitated sulphur and the insoluble lead sulphate are separated by filtration, the residue being thoroughly washed with distilled water, and the combined filtrate and washings are then acidified with dilute sulphuric acid and titrated with decinormal potassium permanganate. The amount of lead in the solution is calculated from the equivalents :

$$2KMnO_4 \equiv 10FeSO_4 \equiv 5Pb.$$
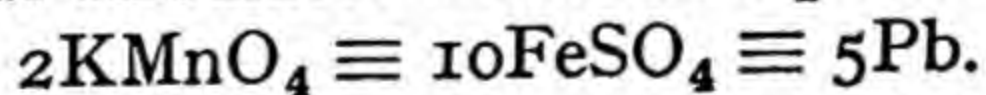
Thus, 31·6 grams of $KMnO_4$ are equivalent to 103·5 grams of Pb ; i.e. 1 litre of 0·1N.$KMnO_4$ is equivalent to 10·35 grams of Pb.

For example, in an experiment, 5·17 grams of lead nitrate were dissolved in distilled water and diluted to 250 c.c. After being completely converted to lead sulphide and reacting with excess of ferric sulphate solution, the resulting ferrous iron solution was diluted to 500 c.c. Suppose also, that, as a mean of three titrations, 50 c.c. of the ferrous iron solution required 31·3 c.c. of 0·1N.$KMnO_4$ for complete oxidation.
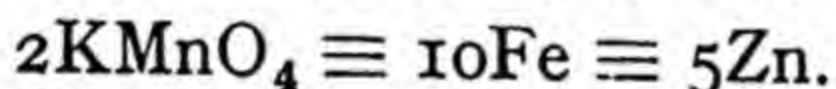
Then, since 1 litre of 0·1N.KMnO$_4$ is equivalent to 10·35 grams of Pb, 31·3 c.c. of 0·1N.KMnO$_4$ are equivalent to 31·3 × 0·01035, or 0·324 grams, Pb.

Therefore, the percentage of lead in lead nitrate is

$$\frac{0·324}{5·17} \times 100, \quad \text{or} \quad 62·7\%.$$

N.B.—This same method may be employed for the estimation of mercury, bismuth, cadmium, copper (though a better method is available for this metal ; see next section, §44), silver, tin, antimony, arsenic, platinum, and gold.

(b) *The Estimation of Zinc in Zinc Sulphate as an Example of a Metal which Forms a Sulphide Soluble in Acid Solution.* In the case of a metal which forms a sulphide *soluble* in acid solution the procedure is along the same lines as in the previous determination, with the additional precaution that the salt solution must be made alkaline with ammonium hydroxide solution. In the case of zinc the zinc sulphate solution is made thoroughly alkaline with NH$_4$OH and kept alkaline while it is being saturated with the hydrogen sulphide. The zinc is then all precipitated as zinc sulphide. The precipitate of ZnS is treated in exactly the same way as the PbS in the previous determination, and the reduced ferric sulphate solution is diluted and titrated with decinormal potassium permanganate solution in the usual way. The amount of zinc in the solution is calculated from the equivalents :

$$2KMnO_4 \equiv 10Fe \equiv 5Zn.$$

Thus, 31·6 grams of KMnO$_4$ are equivalent to 32·7 grams of Zn ; i.e. 1 litre of 0·1N.KMnO$_4$ is equivalent to 3·27 grams of zinc.

The calculation then proceeds in exactly the same way as in the estimation of lead.

44. THE DETERMINATION OF COPPER BY MEANS OF POTASSIUM PERMANGANATE. We have seen that copper may be determined by precipitating all the copper in a soluble copper salt as the insoluble sulphide, and then allowing it to react with excess of ferric sulphate solution and estimating the resulting ferrous sulphate in the usual way. There is, however, another common method employing potassium permanganate, by which this metal can be determined :

By the Replacement Method with Zinc. The method is based upon the fact that a more electro-positive metal, such as zinc, will always replace copper in a solution of a copper

salt. Where zinc is employed the reaction is expressed by the equation :

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

Method. A known weight of pure, crystalline copper sulphate, $CuSO_4.5H_2O$, is dissolved in water and diluted to a convenient volume. A moderately large piece of pure zinc foil (free from arsenic, iron, etc.) is added to the copper solution, and, when the blue colour of the solution has disappeared all the copper will have been precipitated in the metallic condition. Confirmation of the completeness of the reaction may be obtained by testing the solution with a drop of potassium ferrocyanide solution on a white tile : if copper is still unreplaced in the solution, a brown colour will be observed, and the reaction must be continued until this test gives a negative result. The excess zinc is then dissolved by adding dilute sulphuric acid, and the copper is carefully filtered, well washed with distilled water, and dissolved in a mixture of ferric sulphate and sulphuric acid. The ferric sulphate is slowly reduced to the ferrous state according to the equation :

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4.$$
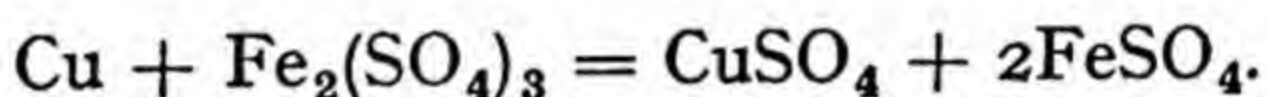
The solution is then diluted to a suitable volume, and the ferrous iron determined in the usual way with decinormal potassium permanganate. The amount of copper is calculated from the equivalents :

$$2KMnO_4 \equiv 10Fe \equiv 5Cu.$$
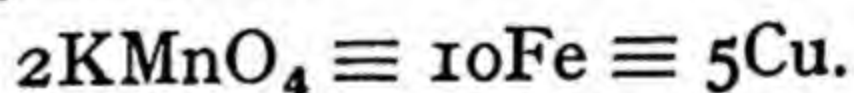
Therefore, 31·6 grams of $KMnO_4$ are equivalent to 31·8 grams of copper, i.e. 1 litre of 0·1N.$KMnO_4$ is equivalent to 3·18 grams of copper.

For example, in an experiment, 4·04 grams of copper sulphate, $CuSO_4.5H_2O$, were dissolved in water, and after the copper had been totally replaced by zinc, and digested with ferric sulphate and sulphuric acid, the resulting solution containing the ferrous sulphate was diluted to 250 c.c. with distilled water. It was found, as a mean of three titrations, that 25 c.c. of this solution required 32·5 c.c. of 0·1N.$KMnO_4$ for complete oxidation.

Then, since 1 litre of 0·1N.$KMnO_4$ is equivalent to 3·18 grams of Cu, it follows that 32·5 c.c. of 0·1N.$KMnO_4$ are equivalent to 0·00318 × 32·5, or 0·1034 gram, of Cu.

Therefore, 250 c.c. of the reduced solution contain 1·034 grams of Cu.

Thus, the percentage of copper in crystallized copper sulphate is

$$\frac{1 \cdot 034}{4 \cdot 04} \times 100, \text{ or } 25 \cdot 6\%.$$

45. THE ESTIMATION OF AVAILABLE OXYGEN IN MANGANESE OXIDES. The 'available oxygen' in an oxide of manganese is the amount of oxygen which is liberated for oxidizing purposes when the oxide is decomposed by acids. There are two main methods of determining this available oxygen :

(a) By decomposing the oxide with HCl and allowing the evolved chlorine to liberate its equivalent of iodine, which is then determined by titration with standard sodium thiosulphate (see § 75) ; or

(b) By decomposing the oxide with H_2SO_4 in the presence of a measured excess of oxalic acid or ferrous sulphate. The amount of oxygen which has oxidized either of these compounds can then be determined by titration with standard potassium permanganate.

The liberation of oxygen, in the cases of the two common ores, is expressed by the reactions :

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2,$$

or

$$2Mn_2O_3 + 4H_2SO_4 = 4MnSO_4 + 4H_2O + O_2.$$
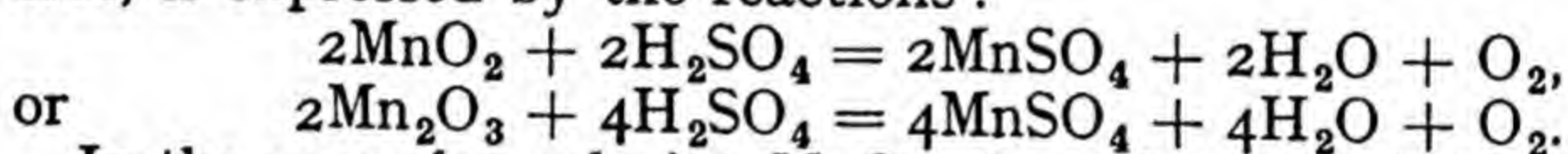
In the case of pyrolusite, MnO_2, the oxidation of the oxalic acid or the ferrous sulphate takes place according to the equations :

$$MnO_2 + (COOH)_2 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2,$$

and
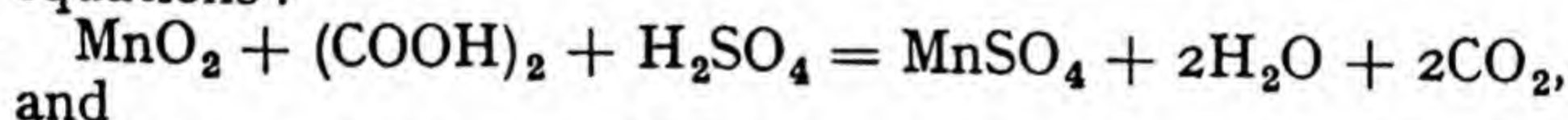
$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O;$$

and in the case of the manganese sesquioxide, the respective reactions are represented by the equations :

$$Mn_2O_3 + (COOH)_2 + 2H_2SO_4 = 2MnSO_4 + 3H_2O + 2CO_2,$$

and

$$Mn_2O_3 + 2FeSO_4 + 3H_2SO_4 = Fe_2(SO_4)_3 + 2MnSO_4 + 3H_2O.$$
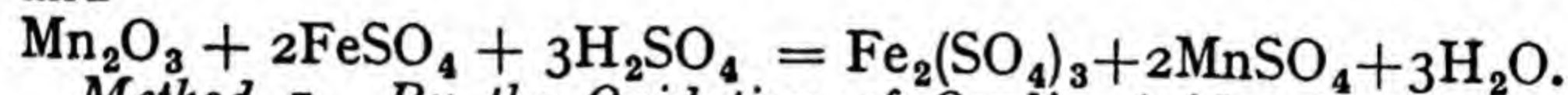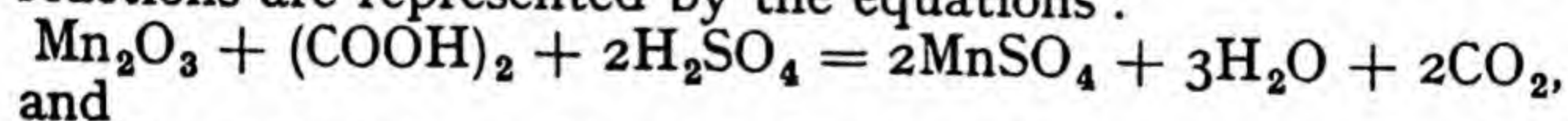
Method 1. By the Oxidation of Oxalic Acid. About 0·5 gram of the finely powdered oxide is taken together with a measured excess of decinormal oxalic acid solution (say 200 c.c.), and then heated with dilute sulphuric acid until all the ore has been decomposed ; the temperature, during this operation, should not be allowed to rise above 80° C. If a white precipitate is observed when the reaction is completed this is probably due to insoluble silicates associated with the manganese ore, and may be neglected. The solution is

allowed to cool, diluted to a suitable volume, and aliquot portions are titrated with decinormal potassium permanganate solution at a temperature of about 60° C.

For example, suppose that the solution contained 0·523 gram of pyrolusite (MnO_2), with 200 c.c. of 0·1N. oxalic acid, and that, after oxidation with dilute sulphuric acid, the resulting solution was diluted to 500 c.c. Further, 100 c.c. of this solution required, as a mean of three titrations, 30·0 c.c. of 0·1N.$KMnO_4$ to completely oxidize the excess oxalic acid.

Then, 500 c.c. of the solution would require 30·0 × 5, or 150 c.c. of 0·1N.$KMnO_4$.

Therefore, the volume of 0·1N. oxalic acid oxidized by the oxygen liberated from the manganese ore is (200 − 150), or 50 c.c.

Now,
$$MnO_2 \equiv (COOH)_2$$
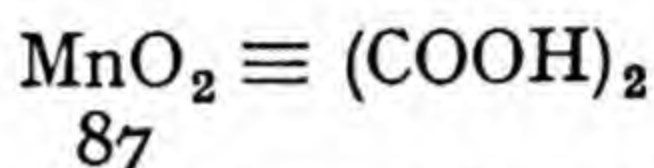$$87$$

Thus 8·7 grams of MnO_2 are equivalent to 1 litre of 0·1N. oxalic acid.

Therefore, 50 c.c. of 0·1N. oxalic acid are equivalent to 0·0087 × 50, or 0·475 gram, of MnO_2.

Thus, the percentage of MnO_2 in the sample of pyrolusite is $\frac{47·5}{0·523}$, or 90·8%. The answer may be expressed that the pyrolusite contains 90·8% of MnO_2, or it may be put in terms of oxygen directly.

Thus, since 87 grams of pure MnO_2 liberate 16 grams of 'available oxygen', it follows that *1 gram of the pyrolusite will liberate 0·908 × $\frac{16}{87}$, or 0·167 gram, of ' available oxygen '.*

Method 2. By the Oxidation of Ferrous Sulphate. The manganese dioxide must first of all be dried in the steam oven. About 1 gram of the dioxide is then finely crushed, weighed accurately, and added to a solution containing a known weight of ferrous ammonium sulphate and excess of dilute sulphuric acid. The mixture is heated gently until all the ore has dissolved (here, again, a white precipitate of insoluble siliceous matter may be neglected). The solution is cooled, the flask being fitted with a bunsen valve to prevent the entrance of atmospheric oxygen (though the risk of oxidation is not so great when ferrous ammonium sulphate is employed as it would be with ordinary ferrous sulphate, it is best to be absolutely certain), and the solution is then diluted with air-free distilled water to a suitable volume.

Aliquot portions of this solution are titrated with $0.1N.KMnO_4$ and the excess ferrous iron estimated. In this reaction

$$MnO_2 \equiv 2Fe$$
$$87 \qquad 112$$
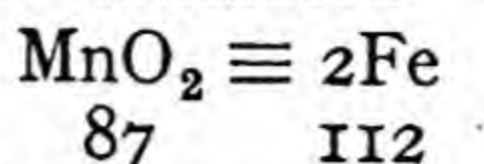
Thus 87 grams of MnO_2 are equivalent to 112 grams of Fe.

For example, suppose that 0.976 grams of ore were taken. The weight of ferrous ammonium sulphate was 16.45 grams, i.e. $\dfrac{16.45}{7}$, or 2.35 grams, of ferrous iron (see § 35).

After the oxidation had been completed the solution was diluted to 500 c.c. with air-free distilled water, and, as a mean of three titrations, 50 c.c. of the diluted solution required 21.7 c.c. of $0.1N.KMnO_4$ for the complete oxidation of the residual ferrous iron.

Therefore, 500 c.c. of the diluted solution would require 217 c.c of $0.1N.KMnO_4$.

But 217 c.c. of $0.1N.KMnO_4$ are equivalent to 0.0056×217, or 1.215 gram, Fe.

Therefore, $(2.35 - 1.215)$, or 1.135 grams, of Fe have been oxidized by the manganese peroxide from the ferrous to the ferric condition.

But 1.135 grams of Fe are equivalent to $\dfrac{87}{112} \times 1.135$, or 0.888 gram, MnO_2.

Therefore, the percentage of MnO_2 in the ore is $\dfrac{0.888}{0.976} \times 100$, or *90.9% MnO₂* ; i.e. the ' available oxygen ' in 1 gram of the manganese dioxide is $0.909 \times \dfrac{16}{87}$, or *0.168 gram*.

46. THE ESTIMATION OF NITRITES. The estimation is based upon the fact that nitrites are decomposed by dilute acids with the formation, in solution, of nitrous acid ; e.g.

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2.$$
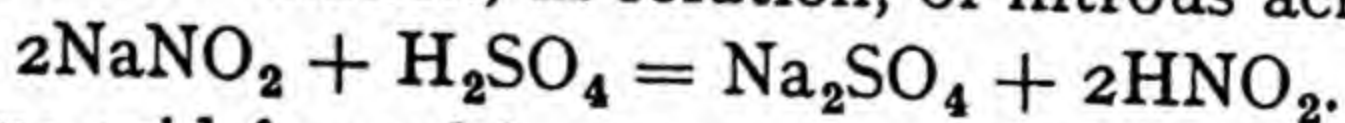
The nitrous acid formed is extremely unstable and splits up, even in dilute solutions, into nitric acid, nitric oxide, and water, viz. :

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$
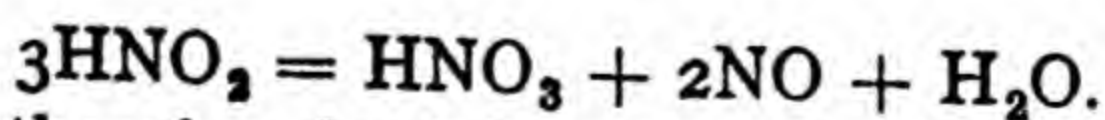
Care must therefore be taken to keep the solution as cool as possible, and any smell of oxides of nitrogen will show that the nitrous acid is being decomposed. Provided, however, that the solution is kept cool, and as long as other oxidizable compounds are absent, the nitrous acid may be

5

estimated by titration with standard potassium permanganate. The reaction proceeds according to the equation :

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$
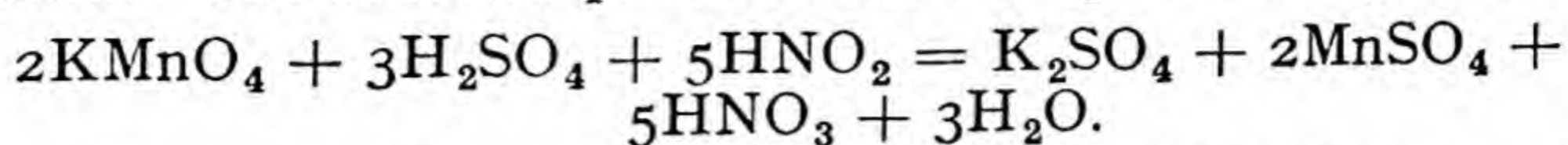
The nitrous is thus oxidized to nitric acid by the permanganate.

In the reaction $2KMnO_4 \equiv 5HNO_2$

$$316 \qquad 235$$

Therefore, 1 litre of o·1N.$KMnO_4$ is equivalent to 2·35 grams of HNO_2.

Example. To Determine the Percentage of Pure KNO_2 in Potassium Nitrite. A known weight of stick potassium nitrite is dissolved in water and made up to a convenient volume with distilled water, and aliquot portions of this solution are titrated with decinormal potassium permanganate solution. This titration must be carried out with great care. 25 c.c. of the nitrite solution are transferred to a small flask and about 10 c.c. of the decinormal permanganate are run in from the burette ; a few drops of dilute sulphuric acid are then added and the mixture shaken gently. Unless the nitrite solution is very dilute the permanganate will be decolorized. More $KMnO_4$ is then run in in small quantities, allowing the mixture to stand for some time after each addition, until a faint pink colour persists ; more dilute sulphuric acid must also be added if necessary, and great care must be taken to ensure that no nitric oxide is liberated in the titration. As the reduction is extremely slow, as the 'end-point' is approached, considerable judgment is required in adding the $KMnO_4$, and in allowing the mixture to stand between the additions of the $KMnO_4$. Three accurate, concordant results are obtained and the percentage of KNO_2 in the nitrite calculated from the equivalents :
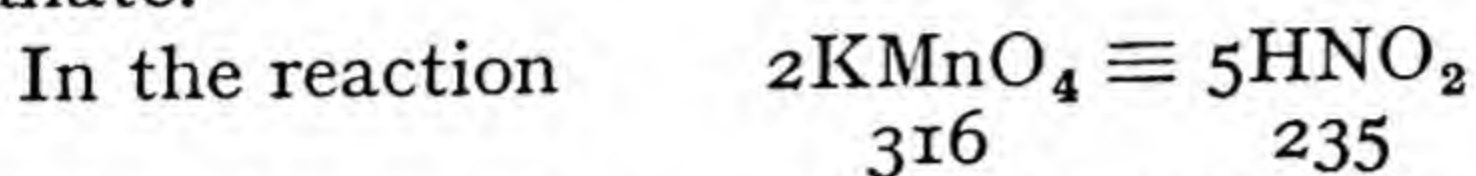
$$2KMnO_4 \equiv 5HNO_2 \equiv 5KNO_2$$

$$316 \qquad\qquad 425$$
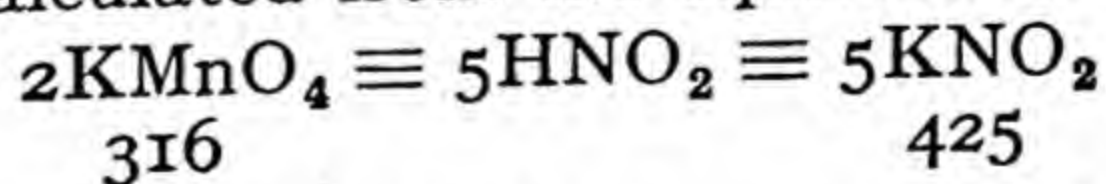
Thus, 1 litre of o·1N.$KMnO_4$ is equivalent to 4·25 grams of KNO_2.

For example, in an experiment, 2·123 grams of stick potassium nitrite were dissolved in distilled water and made up to 500 c.c. As a mean of three concordant titrations, 25 c.c. of the nitrite solution required 25·6 c.c. of o·1N.$KMnO_4$ for complete oxidation.

Then, since 1 litre of o·1N.$KMnO_4$ is equivalent to 4·25

grams of KNO_2, 25·6 c.c. of 0·1N.$KMnO_4$ will be equivalent to 25·6 × 0·00425, or 0·109 gram, of KNO_2.

Therefore, the amount of KNO_2 in 500 c.c. of the solution is 0·109 × $\dfrac{500}{25}$, or 2·076 grams.

Thus the percentage of KNO_2 in the potassium nitrite is

$$\dfrac{2·076}{2·123} \times 100, \text{ or } 97·8\%.$$

47. THE DETERMINATION OF PERSULPHATES. The salts of any of the persulphuric acids may be estimated either by allowing them to react with potassium iodide and titrating the liberated iodine with standard sodium thiosulphate (see § 72), or by allowing them to oxidize a ferrous salt to the ferric state and then estimating the change by means of standard potassium permanganate.

The reactions of the persulphuric acids with ferrous sulphate are as follow :

Permonosulphuric acid :

$$H_2SO_5 + 2FeSO_4 = Fe_2(SO_4)_3 + H_2O.$$

Perdisulphuric acid :

$$H_2S_2O_8 + 2FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4.$$
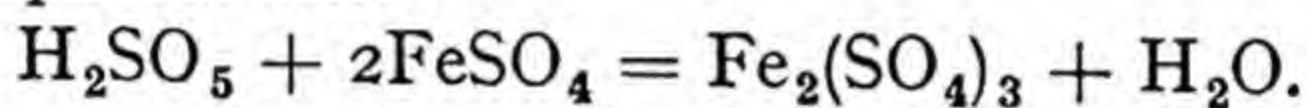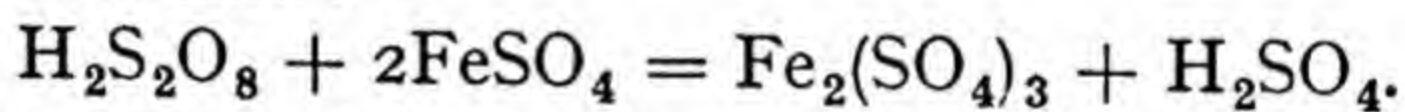
It will be observed that, in each case, the molecular weight of the persulphuric acid will oxidize 2 × 56, or 112 grams, of iron from the ferrous to the ferric condition.

Method. A given volume of the persulphate solution (or a known weight of a persulphate dissolved in a suitable volume of water *) is allowed to react with a measured excess of ferrous ammonium sulphate in the presence of a sufficiently large volume of dilute sulphuric acid. The solution is then cooled, diluted to a convenient volume, and aliquot portions of this solution are titrated with 0·1N.$KMnO_4$.

Example. A solution of sodium hydrogen sulphate in cold sulphuric acid was electrolyzed, with the formation of sodium perdisulphate. The formation of this salt occurs in the following manner :

The acid sodium sulphate is ionized :

$$NaHSO_4 \rightleftharpoons \overset{+}{Na} + \overset{-}{HSO_4}.$$
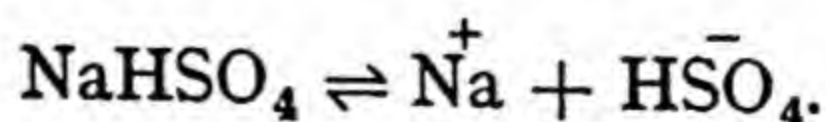
The $\overset{-}{HSO_4}$ ions are discharged at the anode, and, as the

* The solution is very unstable and must be kept cold.

concentration of the ions is quite high, two $\overline{H}SO_4$ groups combine to form perdisulphuric acid, viz. :

$$2\overline{H}SO_4 = H_2S_2O_8.$$
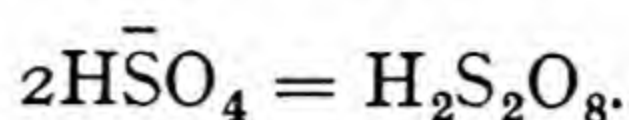
The sodium salt of this acid, $Na_2S_2O_8$, is then formed as a secondary product.

It is required to find the amount of sodium perdisulphate formed in the reaction.

Method. 100 c.c. of the electrolyzed solution were transferred, by means of a pipette, to a small flask containing 11·620 grams of pure recrystallized ferrous ammonium sulphate dissolved in dilute sulphuric acid ; i.e. the solution contained $\dfrac{11\cdot620}{7}$, or 1·660 grams, of iron in the ferrous state (see § 35). The mixture was warmed gently, cooled, and diluted to 250 c.c. As a mean of three titrations, it was found that 25 c.c. of this solution required 18·3 c.c. of 0·1N.$KMnO_4$ for complete oxidation. Therefore, 250 c.c. of the solution would require 183 c.c. of 0·1N.$KMnO_4$ for complete oxidation.

And 183 c.c. of 0·1N.$KMnO_4$ are equivalent to $183 \times 0\cdot0056$, or 1·025 gram, Fe.

Therefore, (1·660 − 1·025), or 0·635 gram, Fe has been oxidized from the ferrous to the ferric state,

and
$$\underset{238}{H_2S_2O_8} \equiv \underset{}{Na_2S_2O_8} \equiv \underset{112}{2Fe}$$
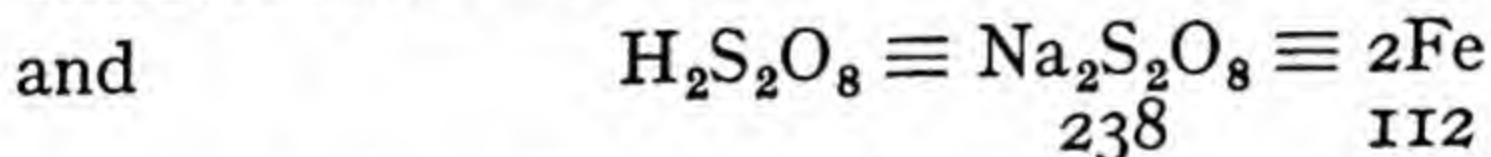
i.e. 112 grams Fe are equivalent to 238 grams of $Na_2S_2O_8$.

Therefore, 0·635 gram Fe is equivalent to $\dfrac{238}{112} \times 0\cdot635$ grams $Na_2S_2O_8$, and this amount of $Na_2S_2O_8$ was contained in 100 c.c. of the electrolyzed solution ; therefore, 1 litre of the sodium hydrogen sulphate solution would give, on electrolysis, $\dfrac{238}{112} \times 0\cdot635 \times 10$, or *16·0 grams, of sodium perdisulphate.*

In a similar manner the amount of permonosulphuric acid, H_2SO_5, in a solution, could be estimated, and, in general, any oxidizing agent may be determined by allowing it to react with a known excess of ferrous ammonium sulphate and then determining the residual ferrous iron by titration with standard potassium permanganate. The oxidizing agent in question, however, must not be contaminated by traces of other oxidizing agents.

48. THE OXIDIZING ACTION OF POTASSIUM PERMANGANATE IN ALKALINE OR NEUTRAL SOLUTION. In alkaline or neutral solution, potassium permanganate is reduced to a hydrated form of manganese dioxide, and *two* molecules of the permanganate yield *three* atoms of ' available oxygen '. The reaction may be represented by the equation :

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O.$$
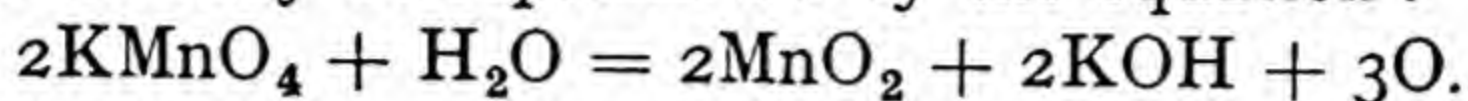
Since potassium permanganate is derived from dimanganese heptoxide, the reduction may be represented as follows :

$$Mn_2O_7 \rightarrow 2MnO_2 + 3O.$$
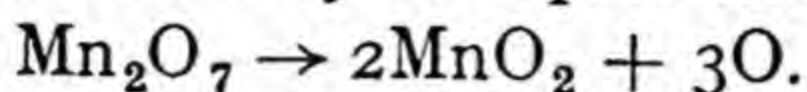
It will be noticed, from the first equation, that, even if the solution is neutral at the start, it becomes alkaline as the reaction proceeds owing to the formation of KOH. It is only necessary, however, to have a strictly neutral solution in rare cases.

In such a case the solution is kept neutral by the addition of magnesium sulphate, which forms insoluble magnesium hydroxide, with the KOH formed during the oxidation.

The Determination of Formic Acid. The most frequent determination made with $KMnO_4$ in alkaline solution is that of Formic Acid. If the formic acid is converted into sodium formate by the addition of excess of sodium carbonate it is oxidized to carbon dioxide ; the reaction may be represented by the equation :

$$2KMnO_4 + 3H.COOH = 2KOH + 2MnO_2 + 2H_2O + 3CO_2.$$
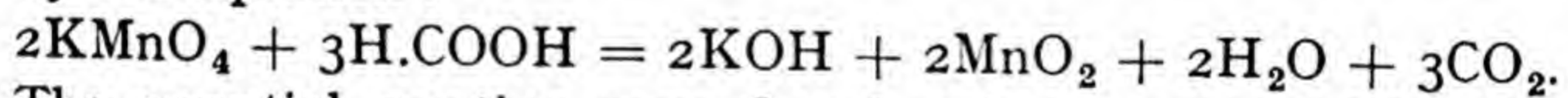
The essential reaction may therefore be represented by the equation :

$$H.COOH + O \rightarrow H_2O + CO_2.$$
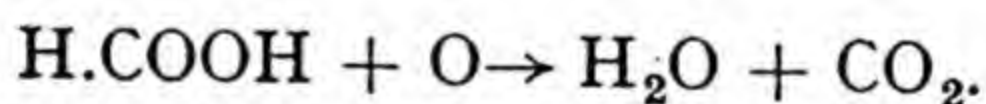
It is preferable, where $KMnO_4$ is used in alkaline solution, to express the strength directly in grams per litre and not in terms of normality.

For example, an ordinary decinormal solution of $KMnO_4$ as used for oxidation purposes in acid solution would not be a decinormal solution for oxidation in alkaline solution (see § 5). The strength of the formic acid can then be determined from the equivalents :

$$2KMnO_4 \equiv 3H.COOH$$
$$316 \qquad 138$$
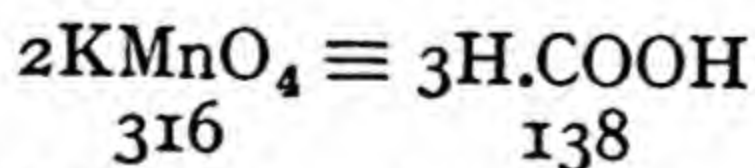
For example, in an experiment to determine the percentage strength of a solution of formic acid, 9·50 grams of the concentrated formic acid were diluted to 250 c.c. with distilled water. *Hot,* aliquot portions of 25 c.c. of this solution were

then titrated *very slowly* with KMnO₄ solution containing 31·6 grams of KMnO₄ per litre. As a mean of three titrations, it was found that 28·5 c.c. of the permanganate solution were required to completely oxidize the formic acid.

Now, 316 grams of KMnO₄ are equivalent to 138 grams of H.COOH,

∴ 28·5 × 0·0316 grams of KMnO₄ are equivalent to

$$\frac{138}{316} \times 28\cdot5 \times 0\cdot0316, \text{ or } 0\cdot393 \text{ gram, of H.COOH.}$$

Therefore, 250 c.c. of the diluted formic acid solution contain 3·93 grams of H.COOH.

Thus the percentage of H.COOH in the sample of formic acid is

$$\frac{3\cdot93}{9\cdot50} \times 100, \text{ or } \textit{41·4\%, H.COOH.}$$

SUGGESTED EXPERIMENTS ON CHAPTER III

1. Given a decinormal solution of potassium permanganate, determine the percentage purity of a specimen of iron wire.

2. By means of decinormal potassium permanganate solution determine the percentage of iron in iron alum.

3. You are provided with a solution of a ferric salt, and are asked to reduce it to the ferrous state with zinc and sulphuric acid. At ten minutes' intervals, during the reduction, withdraw aliquot portions of the solution, and titrate with decinormal potassium permanganate. From the titration values determine the percentage of ferric salt reduced to the ferrous state. Plot your results in the form of a curve. N.B.—The actual strength of the ferric solution need not be known : the ferric solution is titrated with the permanganate at the commencement of the reaction (in case there is any ferrous salt present) and the titration value called n_0 ; the values of n_1, n_2, etc., can then be taken as proportional to the amount of ferrous salt formed.

4. Prepare a cold solution of hydrogen peroxide by treating barium peroxide with excess of dilute sulphuric acid. Estimate the strength of the solution in grams per litre, by means of decinormal potassium permanganate.

5. Given decinormal potassium permanganate, find the strength, in grams per c.c., of the ordinary ' 20 volume ' hydrogen peroxide.

6. You are provided with a decinormal solution of oxalic acid, and are asked to determine the percentage purity of commercial potassium permanganate crystals.

7. By means of decinormal potassium permanganate determine the number of molecules of water of crystallization in (a) hydrated oxalic acid, and (b) ferrous ammonium sulphate.

8. You are provided with pure barium carbonate, dilute sulphuric acid, ammonium oxalate solution, and decinormal potassium permanganate. Find the percentage of barium in the carbonate.

9. Given decinormal potassium permanganate, a hydrogen sulphide

apparatus, and $Fe_2(SO_4)_3$, find the percentage of cadmium in anhydrous cadmium chloride.

10. Given the same reagents as in experiment 9, determine the percentage of nickel in nickel sulphate. How does the determination differ from the preceding estimation ?

11. You are provided with pure zinc-foil, recrystallized cupric chloride, decinormal ferric sulphate (in 2N. sulphuric acid solution), and decinormal potassium permanganate. Find the percentage of copper in the cupric chloride.

12. Potassium nitrate, when heated strongly, decomposes into potassium nitrite and oxygen, according to the equation :

$$2KNO_3 = 2KNO_2 + O_2.$$
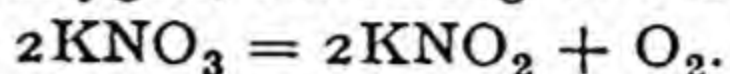
Heat about 2 grams of pure potassium nitrate in a crucible for about half an hour, cool, and dissolve the residue in distilled water, and dilute to a convenient volume. By means of decinormal potassium permanganate determine how far the decomposition of the nitrate has proceeded.

13. You are provided with decinormal solutions of oxalic acid and potassium permanganate, and are asked to determine the percentage of manganese in pure manganese dioxide.

CHAPTER IV

VOLUMETRIC ESTIMATIONS BASED UPON OXIDATION AND REDUCTION METHODS (Part 2)

POTASSIUM DICHROMATE

49. Potassium dichromate, $K_2Cr_2O_7$, like potassium permanganate, reacts in acid solution as an oxidizing agent. Actually, *one* molecule of the dichromate liberates *three* atoms of 'available oxygen'; e.g.

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

The dichromate is thus reduced to potassium sulphate (derived from potassium monoxide, K_2O), and chromic sulphate (derived from chromium sesquioxide, Cr_2O_3).

We may, however, regard potassium dichromate as composed of two oxides, potassium monoxide, K_2O, and chromic anhydride, Cr_2O_6, viz. :

$$K_2Cr_2O_7 \equiv K_2O + Cr_2O_6 ;$$
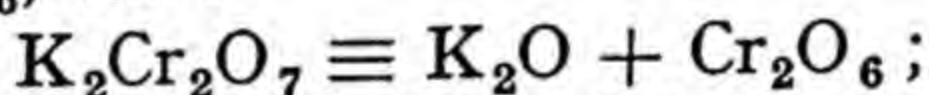
and, since chromic sulphate, $Cr_2(SO_4)_3$, is the salt corresponding to the oxide Cr_2O_3, we may represent the reduction of potassium dichromate by the equation :

$$Cr_2O_6 \rightarrow Cr_2O_3 + 3O.$$

Thus, $$K_2Cr_2O_7 \equiv 3O \equiv 6H,$$
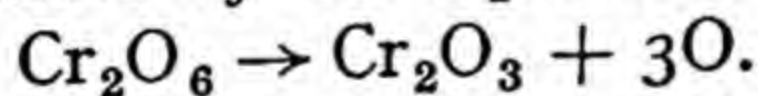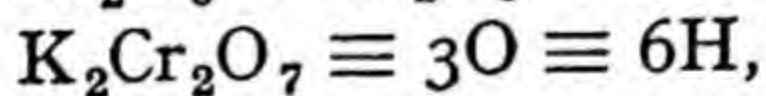
i.e. the chemical equivalent of potassium dichromate, when used as an oxidizing agent in acid solution, is equal to *one-sixth* the molecular weight. A normal solution of $K_2Cr_2O_7$ will therefore contain $\frac{294 \cdot 2}{6}$, or 49·0 grams, of $K_2Cr_2O_7$ per litre.

1 litre of normal potassium dichromate solution will, thus, liberate 8·0 grams of 'available oxygen'.

50. THE STANDARDIZATION OF POTASSIUM DICHROMATE. As in the case of potassium permanganate, decinormal solutions of this reagent are generally used in a determination. In order to prepare an approximately decinormal solution of $K_2Cr_2O_7$, about 6 grams of the pure dichromate are dried by heating gently in a porcelain dish until the solid just fuses, and then powdered in a dry mortar. About 5 grams of the

powdered salt are then weighed accurately and dissolved in distilled water and diluted to 1 litre.

This solution is then standardized by means of ferrous ammonium sulphate. The reaction takes place according to the equation :

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 +$$
$$3Fe_2(SO_4)_3 + 7H_2O ;$$
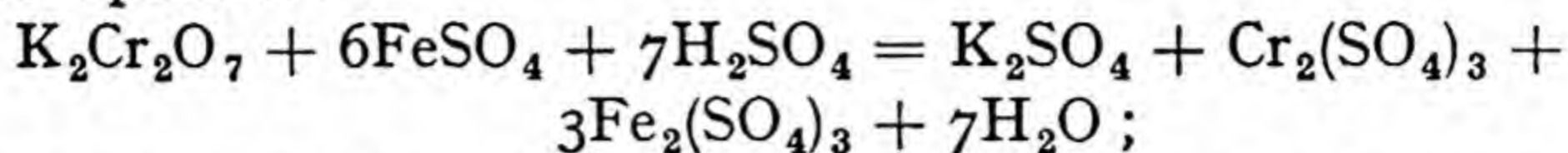
and since 1 litre of decinormal potassium dichromate is equivalent to 8·0 grams of oxygen, it will also be equivalent to 5·6 grams of iron. Thus 1 c.c. of 0·1N.$K_2Cr_2O_7$ will oxidize 0·0056 gram of iron from the ferrous to the ferric state.

Method. A known weight of ferrous ammonium sulphate is dissolved in air-free distilled water and diluted to a convenient volume. Then the amount of iron in the solution will be equal to *one-seventh* the weight of salt taken (see § 35). Aliquot portions of this solution are acidified with dilute sulphuric acid and titrated with the approximately decinormal dichromate using a dilute solution of pure *potassium ferricyanide* (free from the ferrocyanide) as an external indicator. A number of drops of the indicator are placed on a white tile, and, at frequent intervals, a drop of the reacting solutions is withdrawn on a glass rod and brought into contact with the indicator : as long as any ferrous salt is present a blue coloration will be produced owing to the formation of ferric-ferrocyanide (Turnbull's blue), but, as the titration proceeds, the blue colour becomes less and less until, when all the ferrous iron has been oxidized to the ferric state, *no blue coloration is observed* : this stage marks the 'end-point' of the reaction.

For example, suppose that 9·87 grams of pure, recrystallized ferrous ammonium sulphate were dissolved in air-free distilled water and diluted to 250 c.c., and, that, as a mean of three titrations, 25 c.c. of this solution required 23·8 c.c. of the approximately decinormal $K_2Cr_2O_7$ for complete oxidation to the ferric state, in the presence of excess of dilute sulphuric acid.

Then, 250 c.c. of the iron solution would require 238 c.c. of the $K_2Cr_2O_7$, but 250 c.c. of the iron solution contain $\dfrac{9·87}{7}$, or 1·41 grams, of Fe.

Now, 5·6 grams of Fe are equivalent to 1 litre of 0·1N.$K_2Cr_2O_7$.

Therefore, 1·41 grams of Fe are equivalent to $\dfrac{1000}{5\cdot6} \times 1\cdot41$, or 252 c.c., of 0·1N.$K_2Cr_2O_7$.

Therefore, (252 − 238), or 14 c.c., of water must be added to every 238 c.c. of the dichromate solution in order to make it accurately decinormal; i.e. 1 litre of the dichromate solution in order to make it accurately decinormal; i.e. 1 litre of the dichromate solution will require the addition of $\dfrac{14 \times 1000}{238}$, or *59 c.c., of water in order to make it accurately* *decinormal.*

51. DETERMINATIONS INVOLVING THE USE OF POTASSIUM DICHROMATE. Potassium dichromate solution may be employed for any estimation based upon the oxidation of ferrous iron to the ferric state, but, otherwise, its use is not so varied as that of potassium permanganate: for example oxalic acid and oxalates cannot be titrated with it. The solution is, however, much more stable than potassium dichromate: it has no action on rubber, and can be used in the presence of hydrochloric acid; in fact, *whenever ferrous iron has to be estimated in the presence of chlorides potassium dichromate must always be used in preference to the permanganate.* Tin and chromium are among the metals commonly determined by standard potassium dichromate solution.

52. THE ESTIMATION OF FERROUS SALTS. The amount of iron in a ferrous salt can be estimated by employing decinormal $K_2Cr_2O_7$ solution in a manner similar to the standardization of the dichromate with ferrous ammonium sulphate; e.g.:

The Estimation of Iron in Ferrous Chloride. An accurately known weight of ferrous chloride is dissolved in air-free distilled water and diluted to a convenient volume. Aliquot portions of this solution are acidified with dilute HCl and titrated with 0·1N.$K_2Cr_2O_7$ solution, using a dilute solution of potassium ferricyanide as an external indicator (see § 50). The ferrous iron is then calculated from the basis that 1 litre of 0·1N.$K_2Cr_2O_7$ is equivalent to 5·6 grams of iron.

For example, in an experiment, 2·860 grams of ferrous chloride were made up to 250 c.c. As a mean of three titrations, 25 c.c. of this solution, acidified with dilute HCl, required 22·5 c.c. of 0·1N.$K_2Cr_2O_7$ for complete oxidation to the ferric state.

Then, since 1 litre of 0·1N.$K_2Cr_2O_7$ is equivalent to 5·6

grams of Fe, 22·5 c.c. of o·1N.K$_2$Cr$_2$O$_7$ will be equivalent to 0·0056 × 22·5, or 0·126 gram, Fe.

Thus, 250 c.c. of ferrous chloride solution contain 1·26 grams of Fe.

Therefore, the percentage of iron in ferrous chloride is

$$\frac{1·26}{2·86} \times 100, \text{ or } 44\%.$$

53. THE ESTIMATION OF FERRIC SALTS. Ferric salts may be determined by means of standard potassium dichromate solution in a manner similar to the determination of ferric salts by standard potassium permanganate. The ferric salt is reduced to the ferrous salt and the estimation then proceeds as in the case of a ferrous salt. The best methods of reduction, however, are different from those employed in the case of potassium permanganate. Sulphur dioxide and hydrogen sulphide may be used, *but only with dilute solutions*, and the *zinc and acid method must not be employed* since the zinc dissolved in the solution would react with the potassium ferricyanide forming zinc ferricyanide with the consequent obscuration of the 'end-point' of the reaction. There are, however, two methods of reduction where standard K$_2$Cr$_2$O$_7$ is to be employed which are eminently suitable: (a) by means of stannous chloride solution, and (b) with alkaline ammonium bisulphite solution.

(a) *Reduction by Means of Stannous Chloride Solution.* Stannous chloride solution will reduce a ferric salt to the ferrous state according to the equation :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$
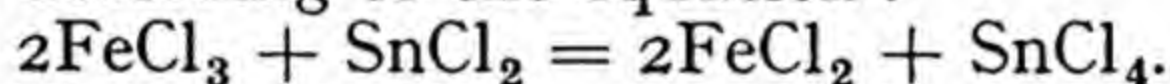
Method. Aliquot portions (25 c.c.) of the ferric iron solution, acidified with dilute HCl, are diluted to 100 c.c. and heated to boiling over a small flame. The stannous chloride solution, which should be quite clear and freshly prepared, is added slowly until the yellow colour of the ferric chloride just disappears : the NH$_4$CNS test must also be made (see § 37). It is very important that only a *slight excess* of the stannous chloride should be added since the stannous chloride reacts with the potassium dichromate and the titration would be affected if excess SnCl$_2$ were present. The slight excess must, therefore, be removed by the addition of a few drops of mercuric chloride solution which precipitates *mercurous* chloride which does not affect the titration, and oxidizes the stannous chloride to stannic chloride which has no effect on the dichromate :

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4.$$
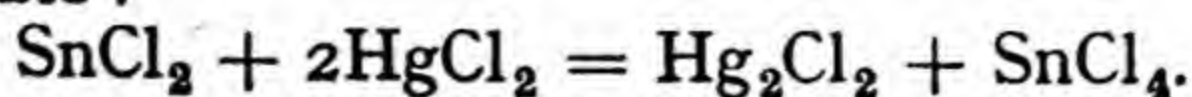
The reduced solution is now titrated with $0.1N.K_2Cr_2O_7$ solution and the iron estimated as in the determination of a ferrous salt.

(b) *Reduction by Means of Alkaline Ammonium Bisulphite Solution.* The ferric iron solution is acidified with dilute HCl, heated to boiling over a small flame, and diluted to a convenient volume. Ammonium hydroxide is then added to the solution until it is slightly alkaline when a reddish-brown precipitate of ferric hydroxide will begin to appear. This precipitate is redissolved by the addition of one or two drops of dilute HCl. About 15 c.c. of a strong solution of ammonium bisulphite, $(NH_4)HSO_3$, are added, and the solution is well shaken and heated to boiling; the same volume of strong sulphuric acid diluted with its own volume of water is then added to the heated solution and the boiling is continued for about twenty minutes to expel all the sulphur dioxide. The solution is then cooled quickly, and diluted to a convenient strength with air-free distilled water. Aliquot portions of this solution are titrated with $0.1N.K_2Cr_2O_7$ solution, using potassium ferricyanide as an external indicator, and the iron estimated as in the determination of a ferrous salt.

For example :

To Determine the Percentage of Iron in Ferric Chloride. 3·83 grams of pure ferric chloride were dissolved in distilled water and diluted to 250 c.c. Portions of 25 c.c. of this solution were acidified with dilute HCl, diluted to 100 c.c., and heated to boiling. $SnCl_2$ solution was then added slowly until the NH_4CNS test showed that no ferric iron was present ; the small excess of $SnCl_2$ was destroyed by the addition of $HgCl_2$ solution as described in (a), and the solution was then titrated with $0.1N.K_2Cr_2O_7$ solution, using potassium ferricyanide as an external indicator.

It was found, as a mean of three determinations, that each 25 c.c. of original iron solution, after reduction to the ferrous state, required 23·5 c.c. of $0.1N.K_2Cr_2O_7$ to give the colour change with potassium ferricyanide.

Therefore, 250 c.c. of the original solution would require 235 c.c. of $0.1N.K_2Cr_2O_7$.

And, since 1 litre of $0.1N.K_2Cr_2O_7$ is equivalent to 5·6 grams of Fe, 235 c.c. of $0.1N.K_2Cr_2O_7$ are equivalent to 235 × 0·0056, or 1·317 grams, Fe.

Therefore, the percentage of iron in ferric chloride is

$$\frac{1.317}{3.83} \times 100, \text{ or } 34.4\%.$$

54. THE ESTIMATION OF IRON IN FERRIC OXIDE (Fe_2O_3). An accurately known weight of very finely powdered ferric oxide is dissolved in strong HCl, the solution being warmed gently on the water bath. When all the oxide has dissolved the solution is allowed to cool and diluted to a convenient volume. Aliquot portions of this diluted solution are reduced with stannous chloride (see § 53), and the reduced solution is titrated with $0 \cdot 1N.K_2Cr_2O_7$ using potassium ferricyanide as an external indicator.

For example, 1·640 grams of the powdered oxide were dissolved in strong HCl and the solution diluted to 250 c.c. It was found that 25 c.c. of the solution, after reduction with $SnCl_2$ and the removal of the excess $SnCl_2$ by $HgCl_2$, required 20·5 c.c. of $0 \cdot 1N.K_2Cr_2O_7$ solution to oxidize the iron from the ferrous to the ferric state.

Therefore, 250 c.c. of the diluted iron solution, after reduction, would require 205 c.c. of $0 \cdot 1N.K_2Cr_2O_7$.

And since 1 litre of $0 \cdot 1N.K_2Cr_2O_7$ is equivalent to 5·6 grams of Fe, 205 c.c. of $0 \cdot 1N.K_2Cr_2O_7$ would be equivalent to 205 × 0·0056, or 1·148 grams, of Fe.

Therefore, the percentage of iron in the ferric oxide is

$$\frac{1 \cdot 148}{1 \cdot 640} \times 100, \text{ or } 70\%.$$

55. TO FIND THE REDUCING POWER OF A SOLUTION OF STANNOUS CHLORIDE. Aliquot portions of the stannous chloride solution are allowed to react with excess of ferric chloride solution acidified with dilute HCl. The amount of iron reduced to the ferrous state is determined by titration with decinormal dichromate solution, and the equivalent amount of stannous chloride deduced from the equation :

$$\underset{190}{SnCl_2} + 2FeCl_3 = SnCl_4 + 2FeCl_2.$$
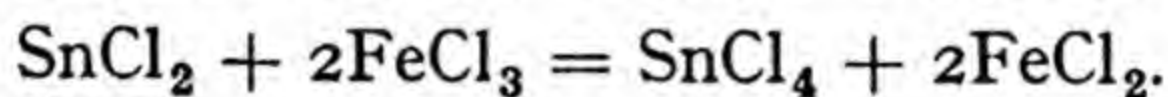
Thus, 190 grams of $SnCl_2$ are equivalent to 2 × 56 grams of Fe.

For example, suppose that 25 c.c. of the $SnCl_2$ solution were allowed to react with excess of ferric chloride solution acidified with dilute HCl, and that 21·4 c.c. of $0 \cdot 1N.K_2Cr_2O_7$ were required to oxidize the ferrous chloride formed by reduction with the stannous chloride.

Then, since 1 litre of decinormal dichromate is equivalent to 5·6 grams of Fe, 21·4 c.c. of decinormal dichromate would be equivalent to 21·4 × 0·0056, or 1·198 grams of Fe.

Therefore, 25 c.c. of the $SnCl_2$ solution will reduce 1·198

grams of Fe from the ferric to the ferrous state ; i.e. 1 c.c. of the SnCl$_2$ solution will reduce $\dfrac{1 \cdot 198}{25}$, or 0·048 gram, of iron.

The reducing power of the stannous chloride solution is thus expressed in terms of iron, viz. :

1 c.c. of the stannous chloride solution will reduce 0·048 gram of iron from the ferric to the ferrous condition.

56. THE DETERMINATION OF TIN IN STANNOUS SALTS. The estimation of tin in a stannous salt is performed in the same way as the reducing power of a solution of stannous chloride was determined in the previous paragraph. The stannous salt, acidified with HCl, is allowed to react with an excess of ferric chloride solution and the amount of iron reduced to the ferrous state is determined by titration with decinormal dichromate in the usual manner. The reaction takes place according to the equation (in the case of stannous chloride) :

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2 \; ;$$
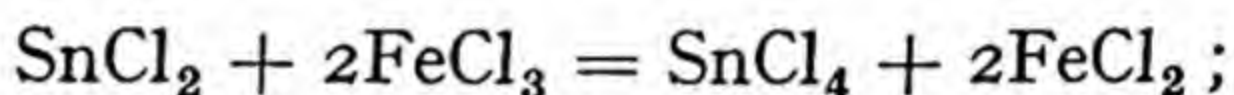
and here 119 grams of tin are equivalent to 2 × 56 grams of iron ; thus 1 litre of 0·1N.K$_2$Cr$_2$O$_7$ solution, which is equivalent to 5·6 grams of Fe, is also equivalent to 5·95 grams of Sn.

For example, 1·639 grams of a stannous salt were dissolved in dilute HCl and diluted to 250 c.c. 25 c.c. of this solution were allowed to react with excess of ferric chloride solution, and the reduced iron was found to require 17·5 c.c. of 0·1N.K$_2$Cr$_2$O$_7$ solution for complete oxidation.

Therefore, 250 c.c. of the original SnCl$_2$ solution would require 175 c.c. of 0·1N.K$_2$Cr$_2$O$_7$ for complete oxidation.

Therefore, 250 c.c. of the original stannous salt solution would require 175 c.c. of 0·1N.K$_2$Cr$_2$O$_7$.

Now, 1 litre of 0·1N.K$_2$Cr$_2$O$_7$ is equivalent to 5·95 grams of Sn.

Therefore, 175 c.c. of 0·1N.K$_2$Cr$_2$O$_7$ would be equivalent to 175 × 0·00595, or 1·036 grams of Sn.

Thus, the percentage of tin in the stannous salt is

$$\frac{1 \cdot 036}{1 \cdot 639} \times 100, \text{ or } 63 \cdot 2\%$$

57. THE ESTIMATION OF CHROMIUM. Chromium may be estimated by converting the chromium compound into a chromate and allowing the solution of this salt to react with an excess of ferrous ammonium sulphate. The determination depends upon the fact that, in the presence of dilute sulphuric

acid, the chromate oxidizes the ferrous salt to the ferric condition, viz. :

$$2K_2CrO_4 + 6FeSO_4 + 8H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O.$$
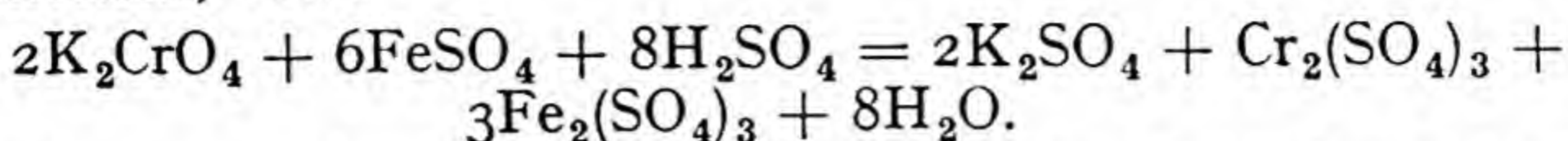
Thus, *one* atom of chromium is capable of oxidizing *three* atoms of iron from the ferrous to the ferric condition, i.e. 52·0 grams of chromium are equivalent to 3 × 56·0, or 168·0 grams, of iron. For example :

To Determine the Percentage of Chromium in Potassium Chromate. A known weight of the pure, crystallized potassium chromate is dissolved in distilled water, acidified with dilute sulphuric acid, and diluted to a convenient volume. A clean, dry, stoppered weighing bottle is filled with pure, recrystallized ferrous ammonium sulphate and weighed. Let this weight be w_1 grams. Small quantities of the ferrous ammonium sulphate are then added to the acidified chromate solution until the chromium is completely reduced and the ferrous salt is present in a slight excess. This can be ascertained by testing a drop of the liquid with dilute potassium ferricyanide solution : when excess of ferrous salt is present a blue coloration will be obtained. Aliquot portions of the solution are then titrated with decinormal dichromate solution using potassium ferricyanide as an external indicator, and the excess iron is thus determined. The weighing bottle is now reweighed. Let this weight be w_2 grams. Then the weight of ferrous salt added to the solution will be $(w_1 - w_2)$ grams. Consequently the weight of iron added to the chromate will be one-seventh of this amount (see § 35). From this amount the excess iron (as determined by titration) is deducted, giving the weight of iron which has been oxidized by the chromate from the ferrous to the ferric state. The chromium is then calculated from the equivalents :

56 grams of Fe $\equiv$ 17·33 grams of Cr.

For example, suppose that, in an experiment, 4·03 grams of K_2CrO_4 were dissolved in water, acidified with dilute sulphuric acid, and diluted to 500 c.c. After reduction it was found that 100 c.c. of this solution required 13·2 c.c. of $0·1N.K_2Cr_2O_7$ for complete oxidation.

Thus, 500 c.c. of the original solution would require 5 × 13·2, or 66·0 c.c., of $0·1N.K_2Cr_2O_7$.

Now, 1 litre of $0·1N.K_2Cr_2O_7$ is equivalent to 5·6 grams of Fe. Therefore, 66·0 c.c. of $0·1N.K_2Cr_2O_7$ are equivalent to 0·0056 × 66, or 0·37 gram, of Fe.

Therefore the amount of iron in excess was *0·37 gram*.

The weight of ferrous ammonium sulphate added to the original solution was 26·95 grams.

Therefore the weight of iron added was one-seventh of this, i.e. 3·85 grams.

Thus, (3·85 − 0·37), or 3·48 grams, of ferrous iron have been required to reduce the potassium chromate solution.

Now, 56 grams of Fe are equivalent to 17·33 grams of Cr, therefore, 3·48 grams of Fe are equivalent to

$$\frac{17\cdot33}{56} \times 3\cdot48, \text{ or } 1\cdot077, \text{ grams of Cr.}$$

Therefore the percentage of chromium in potassium chromate is

$$\frac{1\cdot077}{4\cdot03} \times 100, \text{ or } 26\cdot7\%.$$

SUGGESTED EXPERIMENTS ON CHAPTER IV

1. You are provided with a decinormal solution of potassium permanganate and ferrous ammonium sulphate, and are asked to prepare a decinormal solution of potassium dichromate.

2. Given decinormal potassium dichromate solution determine the respective amounts of ferrous and ferric chloride in a mixture of the two.

3. You are provided with strong HCl, stannous chloride solution, and decinormal potassium dichromate, and are asked to determine the percentage purity of the laboratory ferric oxide.

4. Given the same reagents as in experiment 3, determine the ratio of ferrous to ferric iron in magnetite (Fe_3O_4).

5. You are provided with decinormal potassium dichromate and a solution of ferric chloride, and are asked to determine the strength of a given solution of stannous chloride.

6. Determine the percentage purity of the laboratory potassium chromate by means of a decinormal solution of potassium dichromate.

CHAPTER V

VOLUMETRIC ESTIMATIONS BASED ON OXIDATION AND REDUCTION METHODS (PART 3)

IODOMETRY

58. Iodine is frequently used in volumetric analysis as an indirect oxidizing agent. The method is based upon the fact that free iodine, in the presence of water and certain substances which can be easily oxidized, combines with the hydrogen of the water liberating ' available oxygen '. Regarding the iodine as an oxidizing agent the essential reaction may be represented by the equation :

$$I_2 + H_2O = 2HI + O$$
$$2 \times 127 \qquad\qquad 16$$
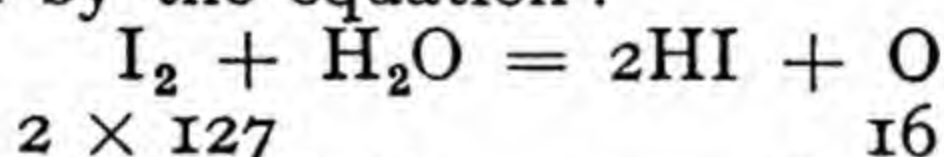
Thus, 127 grams of iodine are equivalent to 8 grams of oxygen ; i.e. a normal solution of iodine will contain 127 grams of pure iodine per litre of solution. In practice, a decinormal iodine solution is found to be the most convenient strength of solution to use ; i.e. a solution containing 12·7 grams of pure iodine per litre. Thus a decinormal iodine solution may be regarded as a decinormal solution of ' available oxygen ' ; i.e. 1 litre of decinormal iodine solution will liberate from the water 0·8 gram of ' available oxygen '.

The ' end-point ' in any iodometric determination may be very accurately indicated by means of dilute starch solution. Starch, when brought into contact with iodine in solution, gives a deep blue coloration due to the formation of an unstable iodine derivative of starch, the exact composition of which is uncertain. This compound, owing to its unstable nature, behaves exactly like free iodine, just as if no starch were present. The ' end-point ' is indicated by the disappearance of the blue colour when free iodine is being titrated by either standard As_4O_6 solution or by standard sodium thiosulphate, $Na_2S_2O_3$.

The Preparation of the Starch Solution. A small quantity of pure starch is mixed into a paste with a little cold water. Boiling water is then poured on to the paste, the solution is stirred, and a colloidal solution of starch results. This solution, when cooled, is ready to be employed as the indicator in any iodometric determination.

6

N.B.—The starch solution should never be kept more than one day ; a fresh solution should be prepared each day.

59. DECINORMAL IODINE SOLUTION. An approximately decinormal iodine solution can be prepared by weighing accurately 12·7 grams of pure, resublimed iodine, adding about 20 grams of pure potassium iodide (iodine is very slightly soluble in water but dissolves readily in a solution of its potassium compound), dissolving in distilled water, and diluting to 1 litre in a graduated flask. It is better, however, to prepare an iodine solution slightly stronger than deci-normal, determine its strength accurately by one of the two alternative methods described below, and then dilute the solution to the required concentration.

N.B.—The standard iodine solution, when prepared must be kept in a stoppered bottle in the dark.

THE STANDARDIZATION OF AN IODINE SOLUTION

(a) *By means of Standard Sodium Thiosulphate Solution.* Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, reacts with iodine, forming sodium iodide and sodium tetrathionate according to the equation :

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$
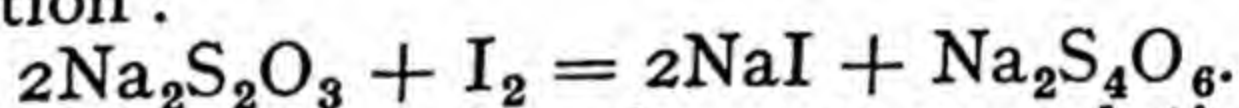
The reaction, taking place in aqueous solution, is one in which the iodine plays the part of an indirect oxidizing agent. The mechanism of the reaction may be represented by the following changes :

(i) $I_2 + H_2O = 2HI + O.$
(ii) $2Na_2S_2O_3 + O = Na_2O + Na_2S_4O_6.$
(iii) $2HI + Na_2O = 2NaI + H_2O.$
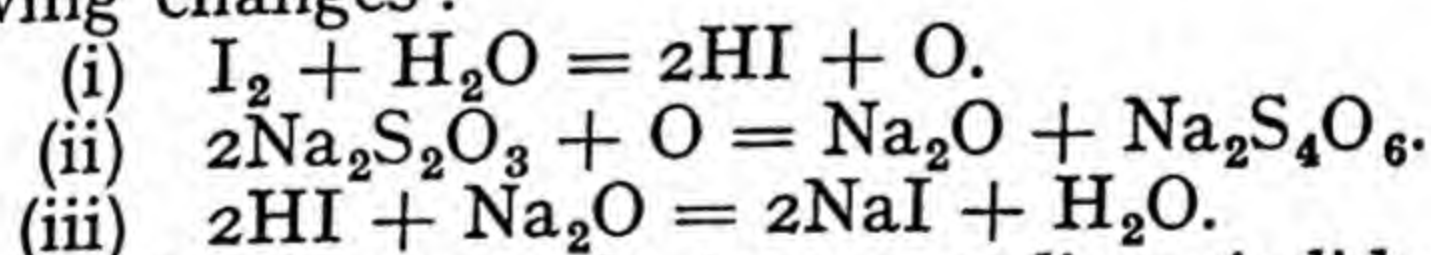
Thus, the final products are sodium iodide and sodium tetrathionate.

Preparation of the Decinormal Sodium Thiosulphate Solution. We have seen that two molecules of sodium thiosulphate are equivalent to one molecule of iodine, viz. :

$$I_2 \equiv 2Na_2S_2O_3 . 5H_2O$$
$$2 \times 127 \qquad 2 \times 248$$
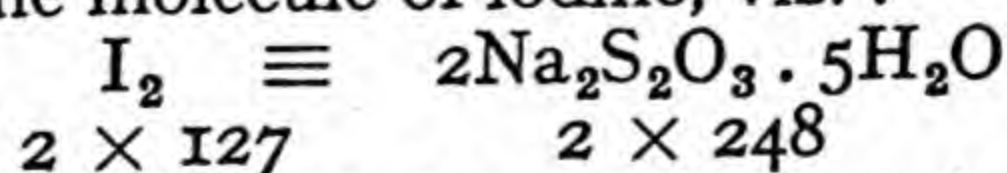
i.e. 12·7 grams of iodine are equivalent to 24·8 grams of hydrated sodium thiosulphate ; thus a decinormal solution of sodium thiosulphate will contain 24·8 grams of $Na_2S_2O_3.5H_2O$ per litre.

In order to prepare a decinormal solution of sodium thio-sulphate it is necessary, therefore, to weigh out accurately

24·8 grams of pure, recrystallized sodium thiosulphate. dissolve it in distilled water, and dilute to one litre. The accuracy of the solution will, of course, depend upon the accuracy of weighing, and a further source of error is introduced by the loss of water of crystallization by evaporation when the crystals are powdered before weighing. It is better, therefore, to prepare a solution of sodium thiosulphate slightly stronger than decinormal and to standardize it by means of an accurately decinormal solution of potassium permanganate or of potassium dichromate. These reagents will liberate free iodine *quantitatively* from potassium iodide in the presence of dilute sulphuric acid, viz. :

$$2KMnO_4 + 8H_2SO_4 + 10KI = 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2.$$

$$K_2Cr_2O_7 + 14HCl + 6KI = 8KCl + Cr_2Cl_6 + 7H_2O + 3I_2.$$
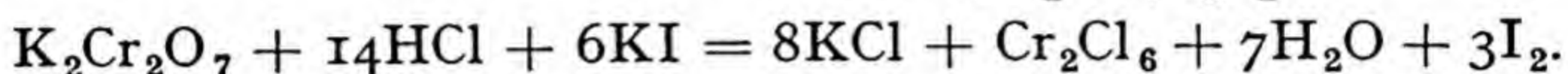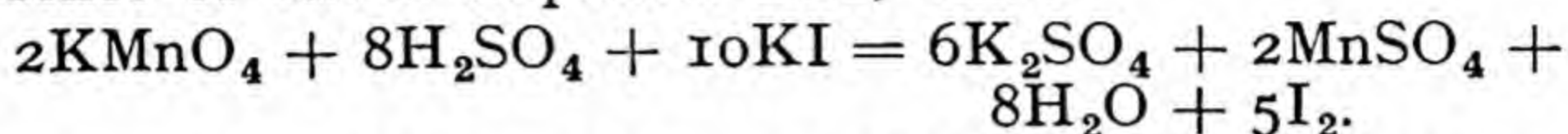
Thus, 100 c.c. of decinormal potassium permanganate (or dichromate) would liberate the equivalent of 100 c.c. of decinormal iodine solution, and this, in turn, would oxidize exactly 100 c.c. of accurately decinormal sodium thiosulphate solution.

For example, suppose that, in the standardization, 100 c.c. of decinormal $KMnO_4$ solution, after treatment with excess potassium iodide, required 95 c.c. of the approximately decinormal $Na_2S_2O_3$ solution to reduce the iodine liberated in the reaction (see below for the actual method of titration), then the normality of the thiosulphate solution is

$$0·1N. \times \frac{100}{95} ;$$

i.e. (100 − 95), or 5 c.c., of water must be added to every 95 c.c. of the thiosulphate solution in order to make it accurately decinormal.

The Titration of the Iodine Solution. Having thus obtained an accurately decinormal solution of sodium thiosulphate, the approximately decinormal solution of iodine may be standardized.

Method. 25 c.c. of the iodine solution are transferred to a small flask and diluted with an equal volume of distilled water. The thiosulphate is then added slowly from the burette until the brown colour of the iodine changes to a faint yellow ; one or two drops of the freshly prepared starch solution are then added, giving the remaining iodine an intense blue colour, and the titration is continued slowly until the blue colour is just

discharged. Three concordant results are obtained and the solution is then standardized.

For example, suppose that 25 c.c. of the iodine solution required a mean volume of 26·0 c.c. of 0·1N.Na$_2$S$_2$O$_3$ to discharge the blue colour of the starch.

Then 1 c.c. of water must be added to every 25 c.c. of the iodine solution, i.e. 40 c.c. per litre, to make it accurately decinormal.

It will be observed that, in any iodometric determination, it is always more convenient to titrate the iodine solution with the thiosulphate, since the starch solution can then be added as the indicator when the reaction is nearly at an end (as denoted by the gradual loss of colour of the iodine solution).

(b) *Standardization by Means of Arsenious Oxide.* Free iodine will oxidize arsenious oxide, in aqueous solution, according to the equation :

$$As_4O_6 + 4I_2 + 4H_2O \rightleftharpoons 8HI + As_4O_{10}.$$
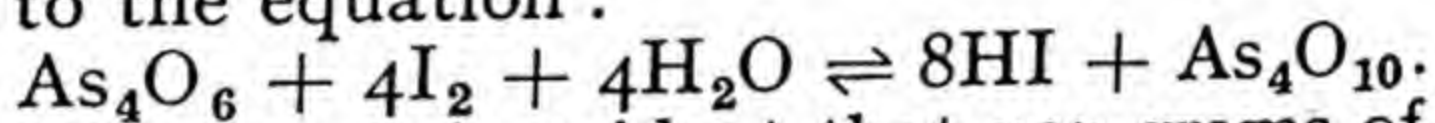
From this equation it is evident that 127 grams of iodine are equivalent to 49·5 grams of arsenious oxide ; i.e. 1 litre of decinormal iodine solution is equivalent to 4·95 grams of As$_4$O$_6$.

As the reaction is reversible it must be performed in the presence of a moderate excess of alkali : this ensures that the hydriodic acid formed in the reaction is neutralized as it is liberated, and reversal is, thus, prevented. As, however, caustic alkalies would react with the free iodine, the best neutralizing agent to employ is *sodium bicarbonate.*

Method. About 5 grams of pure, resublimed As$_4$O$_6$ are weighed accurately and dissolved in distilled water containing about 25 grams of pure sodium bicarbonate. The solution is then diluted to 1 litre and a standard solution in the form of sodium arsenite is thus obtained. Aliquot portions of this solution are then titrated with the approximately decinormal iodine solution, using freshly prepared starch solution as the indicator (or, it may be found more convenient to titrate the iodine solution with the standard arsenite, and to add the starch when the brown colour of the iodine has changed to a pale yellow).

For example, suppose that 5·05 grams of the As$_4$O$_6$ were contained in 1 litre of the arsenite solution, then, since a decinormal As$_4$O$_6$ solution contains 4·95 grams of As$_4$O$_6$ per litre, the normality of the solution will be

$$0·1N. \times \frac{5·05}{4·95}.$$

Suppose, further, that, as a mean of three titrations, 25 c.c. of this solution required 24·5 c.c. of the approximately deci-normal iodine solution to complete the oxidation of the As_4O_6, then the normality of the iodine solution will be

$$0·1N. \times \frac{5·05}{4·95} \times \frac{25}{24·5} ;$$

i.e. 1 litre of the iodine solution contains

$$12·7 \times \frac{5·05}{4·95} \times \frac{25}{24·5}, \text{ or } 16·64 \text{ grams, of iodine.}$$

Now, 12·7 grams of iodine are contained in 1000 c.c. of 0·1N. iodine solution,

Therefore, 16·64 grams of iodine will be contained in

$$1000 \times \frac{16·64}{12·7}, \text{ or } 1310 \text{ c.c., of } 0·1N. \text{ iodine solution.}$$

Therefore (1310—1000), or 310 c.c., of water must be added to 1 litre of iodine solution in order to make it accurately decinormal.

SOME TYPICAL DETERMINATIONS WITH DECINORMAL IODINE SOLUTION

60. THE ESTIMATION OF ARSENIC COMPOUNDS.

(a) *In the Arsenious Condition.* Arsenious compounds are generally estimated as arsenious acid which is oxidized to arsenic acid by iodine in aqueous solution, viz. :

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$
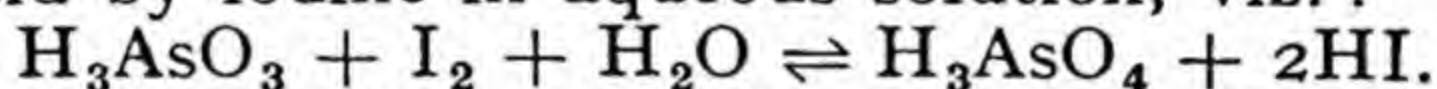
Here, again, a moderate excess of sodium bicarbonate must be present to neutralize the HI formed in the reaction, and thus prevent the reversal of the reaction. The method of determination is exactly the same as the titration of standard iodine by means of As_4O_6 solution (§ 59 (b)) ; e.g.

The Estimation of Sodium Arsenite. A known weight of the arsenite is dissolved in water and diluted to a convenient volume. Aliquot portions of this solution are transferred to a small flask, an equal volume of saturated $NaHCO_3$ solution is added, and the mixture titrated with decinormal iodine, using starch as the indicator. Three concordant results are obtained and the percentage purity of the arsenite calculated from the titration values.

For example, in an experiment to determine the percentage purity of a sample of sodium arsenite, 2·455 grams of the substance were dissolved in water and diluted to 250 c.c. As a mean of three titrations, 25 c.c. of this solution required

23·5 c.c. of o·1N. iodine to completely oxidize the arsenite to the arsenate.

Therefore, 250 c.c. of the solution would require 235 c.c. of o·1N. iodine.

Now, $$I_2 \equiv H_3AsO_3 \equiv Na_3AsO_3$$
$$2 \times 127 \qquad\qquad 192$$
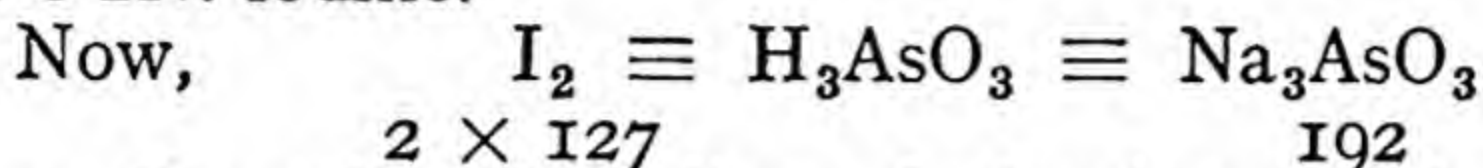
i.e. 1 litre of o·1N. iodine solution is equivalent to 9·60 grams of Na_3AsO_3.

Therefore, 235 c.c. of o·1N. iodine are equivalent to $9·60 \times 0·235$, or 2·256 grams, of Na_3AsO_3.

Thus, the percentage of Na_3AsO_3 in the sample of sodium arsenite is

$$\frac{2·256}{2·455} \times 100, \text{ or } 96\%.$$

(b) *In the ' Arsenic ' Condition.* An ' arsenic ' compound is generally estimated as arsenic acid. It is necessary, however, to reduce the arsenic acid to arsenious acid by means of sulphur dioxide, viz. :

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4.$$
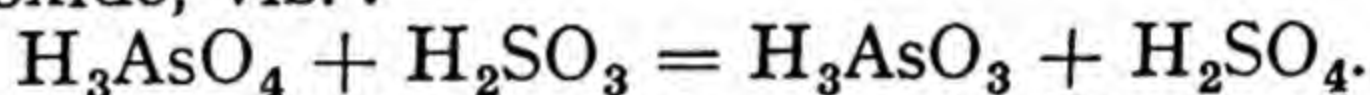
The estimation then proceeds in exactly the same way as for an arsenious compound ; e.g.

The Estimation of Sodium Arsenate. A known weight of the arsenate is dissolved in water ; a little acetic acid is added and the solution boiled for a few minutes to decompose any nitrite, which is a common impurity in sodium arsenate and which would react with the iodine (see § 74). This solution is cooled and diluted to a convenient volume (say 250 c.c. for each 2 grams of arsenate). 100 c.c. of this solution are then saturated with sulphur dioxide ; when reduction is complete the excess sulphur dioxide is boiled off, the solution is cooled, and diluted to, say, 200 c.c., since a small but definite alteration may have taken place. Aliquot portions (50 c.c.) of this solution are then mixed with an equal volume of saturated $NaHCO_3$ solution to neutralize the HI formed in the reaction, and titrated with o·1N. iodine solution, using starch as the indicator.

For example, in an experiment, 2·48 grams of sodium arsenate were dissolved in water, and, after boiling with acetic acid, the solution was diluted to 250 c.c. 100 c.c. of this solution were saturated with SO_2 and then diluted, after cooling, to 200 c.c.

As a mean of three titrations, it was found that 50 c.c. of the reduced solution required 22·5 c.c. of o·1N. iodine solution for complete re-oxidation to the ' arsenic ' condition.

Therefore, 200 c.c. would require 22·5 × 4, or 90·0 c.c., of o·1N. iodine ; i.e. 100 c.c. of the original solution are equivalent to 90 c.c. of o·1N. iodine solution.

Therefore, 250 c.c. of the original solution are equivalent to 90 × 2·5, or 225 c.c., of o·1N. iodine solution.

Now, $I_2 \equiv H_3AsO_3 \equiv H_3AsO_4 \equiv Na_3AsO_4$
2 × 127   208
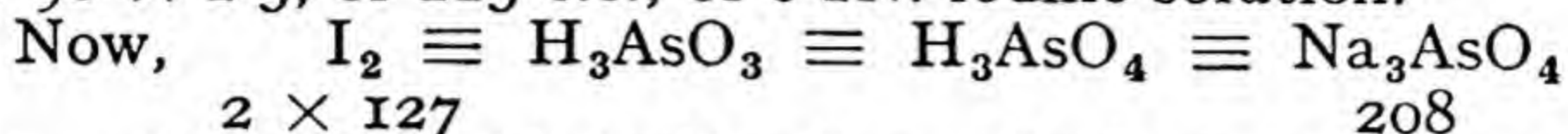
i.e. 1 litre of o·1N. iodine is equivalent to 10·4 grams of Na_3AsO_4.

Therefore 225 c.c. of o·1N. iodine are equivalent to 10·4 × 0·225, or 2·34 grams, of sodium arsenate.

Thus, the percentage of Na_3AsO_4 in the sample of sodium arsenate is

$$\frac{2·34}{2·48} \times 100, \text{ or } 94·4\%.$$

61. THE ESTIMATION OF ANTIMONY.

(a) *In the Antimonious Condition.* Antimonious oxide reacts with free iodine, in aqueous solution, in a manner similar to arsenious oxide, viz. :

$$Sb_4O_6 + 4I_2 + 4H_2O \rightleftharpoons 2Sb_2O_5 + 8HI.$$
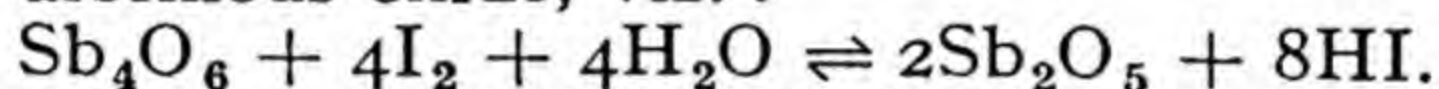
Here, as in the case of antimonious oxide, a moderate excess of sodium bicarbonate must be present to neutralize the HI formed in the reaction, and thus prevent the reverse action taking place. Moreover, whenever an antimonious salt is being determined, *tartaric acid (or sodium potassium tartrate) must also be added to prevent hydrolysis with the consequent precipitation of basic antimony salts.* For example, in the case of antimony chloride, the addition of water would give a white precipitate of antimony oxychloride :

$$SbCl_3 + H_2O = 2HCl + SbOCl.$$
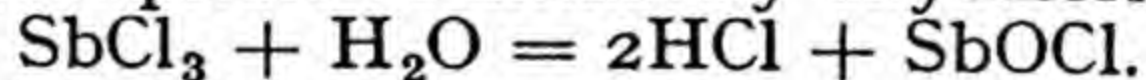
The tartaric acid, however, converts the insoluble oxychloride into the soluble antimonyl tartrate, viz. :

$$2SbOCl + H_2(C_4H_4O_6) = (SbO)_2(C_4H_4O_6) + 2HCl.$$
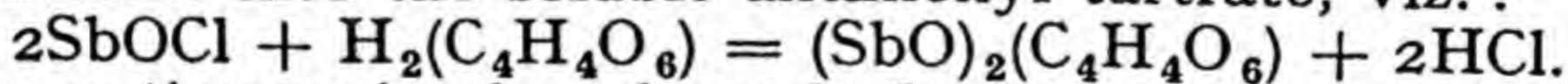
The antimony is, thus, brought back into solution, and the estimation then proceeds exactly as in the case of antimonious compounds. The amount of tartaric acid required may be taken roughly as twice the amount of antimonious compound employed ; e.g.

To Determine the Percentage of Antimony in Tartar Emetic. Tartar emetic, $(SbO)K(C_4H_4O_6).\frac{1}{2}H_2O$, is prepared by the action of potassium hydrogen tartrate on antimonious oxide, viz. :

$$Sb_4O_6 + 4HK(C_4H_4O_6) = 4(SbO)K(C_4H_4O_6) + 2H_2O.$$
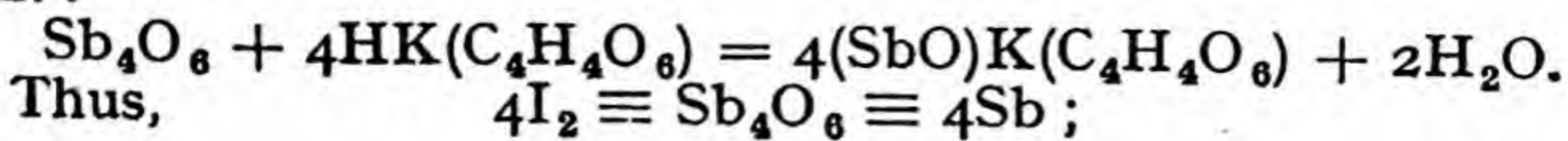
Thus, $4I_2 \equiv Sb_4O_6 \equiv 4Sb$;

i.e. 127 grams of iodine are equivalent to 60·1 grams of Sb, or 1 litre, of 0·1N. iodine solution is equivalent to 6·01 grams of Sb.

For example, suppose that 3·64 grams of tartar emetic were dissolved in water containing about 7 grams of sodium potassium tartrate (see above), and diluted to 250 c.c. 25 c.c. of this solution, to which had been added an equal volume of saturated NaHCO$_3$ solution, were found to require, as a mean of three titrations, 23·8 c.c. of 0·1N. iodine solution to effect the blue coloration with starch solution.

Thus, 250 c.c. of the solution would require 238 c.c. of 0·1N. iodine for complete oxidation.

And, since 1 litre of 0·1N. iodine is equivalent to 6·01 grams of Sb, therefore, 238 c.c. of 0·1N. iodine are equivalent to 6·01 × 0·238, or 1·43 grams, of Sb.

Therefore, the percentage of antimony in the tartar emetic is

$$\frac{1·43}{3·64} \times 100, \text{ or } 39·3\%.$$

(b) *In the Antimonic Condition.* Antimonic compounds are estimated in a manner similar to ' arsenic ' compounds. The compound is, first of all, reduced to the antimonious condition by saturating with SO$_2$ in the presence of dilute HCl ; the excess SO$_2$ is driven off by boiling for a long time, and the solution is made slightly alkaline by means of NaOH (in order to neutralize the HCl). The solution is then cooled, the necessary amount of tartaric acid is added, and the solution is diluted to a convenient volume. The procedure is then the same for an antimonious compound : aliquot portions of the reduced solution are mixed with a moderate excess of NaHCO$_3$ and titrated with 0·1N. iodine solution using starch solution as the indicator.

THE DETERMINATION OF REDUCING AGENTS BY MEANS OF STANDARD IODINE AND SODIUM THIOSULPHATE SOLUTIONS

62. THE ESTIMATION OF SULPHUR DIOXIDE IN AQUEOUS SOLUTION. A fairly accurate estimation of SO$_2$ in *dilute* aqueous solution may be made by means of standard iodine and sodium thiosulphate solutions. With strong solutions of SO$_2$, however, the results would not be accurate, and, in consequence, the solution in question should be diluted considerably before beginning the estimation. The SO$_2$ reacts with free iodine, in aqueous solution, according to the equation :

$$I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI.$$
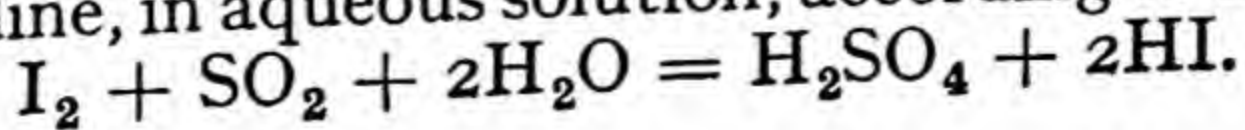
Thus, 127 grams of iodine are equivalent to 32 grams of sulphur dioxide ; i.e. 1 litre of 0·1N. iodine is equivalent to 3·2 grams of SO_2.

Method. The direct titration of the sulphur dioxide solution does not give very dependable results, and it is preferable to allow the SO_2 solution to react with a measured excess of standard iodine solution and then determine the excess iodine by means of standard sodium thiosulphate. A small volume of the dilute SO_2 solution is, therefore, taken ; a measured volume of 0·1N. iodine solution is added, and the excess iodine is determined by titration with $0·1N.Na_2S_2O_3$ solution, using starch as the indicator in the usual way.

For example, in an experiment, 50 c.c. of the SO_2 solution were added to 100 c.c. of 0·1N. iodine solution and the mixture diluted to 250 c.c. with distilled water. Portions of 50 c.c. of this solution were then titrated with $0·1N.Na_2S_2O_3$, starch solution being added as the indicator when the iodine became pale yellow in colour. It was found that a mean volume of 17·2 c.c. of $0·1N.Na_2S_2O_3$ were required.

Then the 250 c.c. of the diluted solution would require 5 × 17·2, or 86·0 c.c., of $0·1N.Na_2S_2O_3$.

Thus (100 − 86), or 14·0 c.c., of 0·1N. iodine solution have been reduced to HI by the SO_2 solution.

Therefore, since 1 litre of 0·1N. iodine is equivalent to 3·2 grams of SO_2, 14·0 c.c. of 0·1N. iodine are equivalent to 3·2 × 0·014, or 0·0448 gram SO_2. Then 50 c.c. of the original SO_2 solution contain 0·0448 gram of SO_2.

Therefore the strength of the original SO_2 solution is 0·0448 × 20, or *0·896 gram, of SO_2 per litre.*

63. THE ESTIMATION OF SULPHUR DIOXIDE IN A SOLUBLE SULPHITE. This determination is carried out in a manner similar to the determination of SO_2 in aqueous solution. A known weight of the sulphite is added to a measured excess of decinormal iodine solution, the mixture is diluted to a convenient volume, and aliquot portions are titrated with decinormal sodium thiosulphate solution, employing starch as the indicator. The excess iodine is thus determined, and the amount of iodine which has been reduced by the sulphite is determined by difference, as in the previous experiment (§ 62).

For example, sodium sulphite reacts with free iodine in aqueous solution according to the equation :

$$Na_2SO_3.7H_2O + I_2 + H_2O = 2HI + Na_2SO_4 + 7H_2O.$$
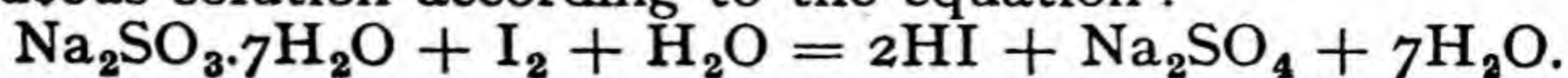
Here, again, 1 litre of 0·1N. iodine is equivalent to 3·2 grams of SO_2; e.g.

To Determine the Percentage of SO_2 in Hydrated Sodium Sulphite. About 1 gram of the sulphite is weighed accurately, added to 200 c.c. of 0·1N. iodine solution, and diluted to 500 c.c. (If the brown colour of the iodine is destroyed on the addition of the sulphite more iodine must, of course, be added.) Portions of 50 c.c. of the diluted solution are then titrated with 0·1N.$Na_2S_2O_3$, using starch as the indicator in the usual way, and the excess iodine is determined from the titration values.

For example, in an experiment, 1·093 grams of the sulphite were added to 200 c.c. of 0·1N. iodine solution and the mixture diluted to 500 c.c.

As a mean of three titrations, 50 c.c. of this solution required 11·7 c.c. of 0·1N.$Na_2S_2O_3$ for complete reduction of the excess iodine.

Therefore 500 c.c. of solution would require 10 × 11·7, or 117 c.c., of 0·1N.$Na_2S_2O_3$.

Thus (200 − 117), or 83·0 c.c., of 0·1N. iodine have been used in oxidizing the sodium sulphite to sodium sulphate. And, since 1 litre of 0·1N. iodine is equivalent to 3·2 grams of SO_2, 83·0 c.c. of 0·1N. iodine will be equivalent to 3·2 × 0·083, or 0·266 gram, of SO_2; i.e. the percentage of SO_2 in hydrated sodium sulphite is :

$$\frac{0·266}{1·093} \times 100, \text{ or } 24·4\%.$$

64. THE ESTIMATION OF HYDROGEN SULPHIDE IN AQUEOUS SOLUTION. Hydrogen sulphide in dilute aqueous solution reacts with free iodine according to the equation :

$$H_2S + I_2 = 2HI + S;$$
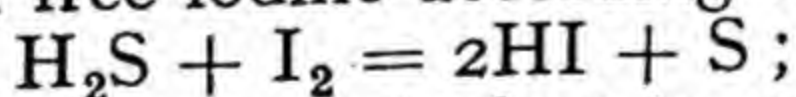
i.e. 127 grams of iodine are equivalent to 17 grams of H_2S, or 1 litre of 0·1N. iodine is equivalent to 1·7 grams of H_2S.

In this reaction, as in the case of sodium thiosulphate, the oxidation actually occurs indirectly through the reaction of the iodine with water. The oxidation is more accurately represented, therefore, by the equations :

$$(i)\ I_2 + H_2O = 2HI + O.$$
$$(ii)\ O + H_2S = H_2O + S.$$
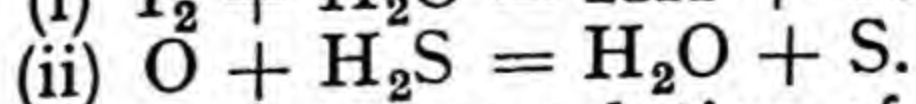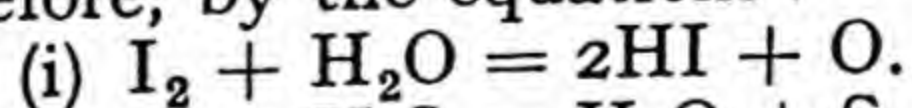
As in the case of an aqueous solution of sulphur dioxide, direct titration is unsatisfactory, and it is preferable to allow the solution of H_2S to react with a measured excess of standard iodine solution and then determine the excess iodine by means

of standard sodium thiosulphate solution. Here, again, accurate results are obtained only with dilute solutions, and it is advisable to dilute the original solution considerably before beginning the actual determination.

For example, in an experiment, 5 c.c. of a H_2S solution were added to 100 c.c. of 0·1N. iodine solution and the solution diluted to 250 c.c. As a mean of three titrations, 50 c.c. of this solution required 17.5 c.c. of 0·1N.$Na_2S_2O_3$ to reduce the excess iodine.

Therefore, 250 c.c. of the solution would require $5 \times 17\cdot5$, or 87·5 c.c., of 0·1N.$Na_2S_2O_3$.

Then, (100 − 87·5), or 12·5 c.c., of 0·1N. iodine have been reduced by the H_2S in the diluted solution.

Then, since 1 litre of 0·1N. iodine solution is equivalent to 1·7 grams of H_2S, therefore 12·5 c.c. of 0·1N. iodine solution are equivalent to $1\cdot7 \times 0\cdot0125$, or 0·02125 gram, of H_2S.

Thus, 5 c.c. of the original H_2S solution contain 0·02125 gram of H_2S. Therefore the strength of the solution is $200 \times 0\cdot02125$, or *4·25 grams, of H_2S per litre.*

Alternative Method for the Estimation of Hydrogen Sulphide in Aqueous Solution employing Standard Alkaline Arsenite Solution. Another method of estimating H_2S in aqueous solution, and one which gives fairly accurate results, is to allow the diluted H_2S solution to react with a measured excess of standard alkaline arsenite solution in the presence of a sufficient excess of HCl to prevent the formation of a colloidal solution of As_2S_3. The reaction takes place according to the equation :

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O.$$
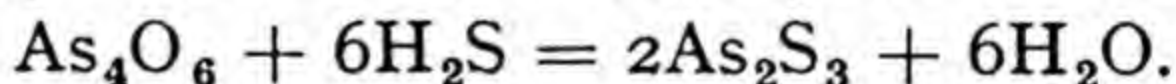
The precipitated arsenious sulphide is filtered off and well washed with distilled water. The filtrate and washings are made alkaline with $NaHCO_3$ (see § 59 (b)), and diluted to a convenient volume. Aliquot portions of this solution are then titrated with 0·1N. iodine in the usual manner. The excess As_4O_6 is thus determined, and the H_2S is determined from the equivalents :

$$As_4O_6 \equiv 6H_2S,$$
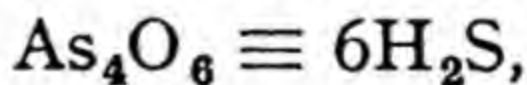
from which it is seen that 1 litre of 0·1N.As_4O_6 solution (4·95 grams of As_4O_6) is equivalent to 2·550 grams of H_2S.

For example, in an experiment, 5 c.c. of a H_2S solution were allowed to react with 100 c.c. of 0·1N.As_4O_6 solution, in the presence of HCl. After the removal of the precipitated As_2S_3 the filtrate and washings were diluted to 250 c.c. It was then found that, as a mean of three titrations, 50 c.c. of

this solution required 18·2 c.c. of o·1N. iodine solution to oxidize the excess As_4O_6.

Then 250 c.c. of the solution would require $5 \times 18·2$, or 91·0 c.c., of o·1N. iodine solution ; i.e. (100 − 91·0), or 9·0 c.c., of o·1N.As_4O_6 solution have been used in reacting with the H_2S in 5 c.c. of the original solution.

Then, since 1 litre of o·1N.As_4O_6 solution is equivalent to 2·550 grams of H_2S, therefore 9·0 c.c. of o·1N.As_4O_6 solution are equivalent to $2·550 \times 0·009$, or 0·0230 gram, of H_2S.

Thus, 5 c.c. of the original solution contain 0·0230 gram of H_2S.

Therefore the strength of the original solution is $200 \times 0·0230$, or *4·60 grams, of H_2S per litre.*

THE DETERMINATION OF OXIDIZING AGENTS BY MEANS OF POTASSIUM IODIDE AND STANDARD SODIUM THIOSULPHATE SOLUTION

Any substance which is capable of oxidizing potassium iodide in aqueous solution to free iodine may be determined volumetrically by allowing that substance to react with excess of potassium iodide, and then titrating the liberated iodine with standard sodium thiosulphate. For example, aqueous solutions of chlorine and bromine may be estimated in this manner ; so may many oxidizing agents, such as persulphates, peroxides, hypochlorites, iodates, bromates, chromates, nitrates, nitrites, vanadates, etc. In fact, this particular branch of iodometry is especially adapted for the determination of those oxidizing agents for which no other more convenient method exists. In general, then, any substance which will liberate iodine *quantitatively* from potassium iodide may be estimated in this manner, though, in a good many cases, the rate of the reaction is slow at ordinary temperatures, and, in such cases, sufficient time must be allowed for the reaction to be completed.

65. THE ESTIMATION OF FREE CHLORINE IN AQUEOUS SOLUTION. A measured volume of the chlorine water is added to an excess of potassium iodide dissolved in a little water. Iodine is liberated immediately according to the equation :

$$2KI + Cl_2 = 2KCl + I_2.$$
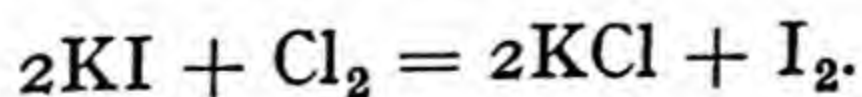
(Actually, the water plays an intermediate part as in the cases of sodium thiosulphate and hydrogen sulphide, viz. :

$$\text{(i) } Cl_2 + H_2O = 2HCl + O.$$
$$\text{(ii) } 2KI + O = K_2O + I_2.$$
$$\text{(iii) } K_2O + 2HCl = 2KCl + H_2O.)$$
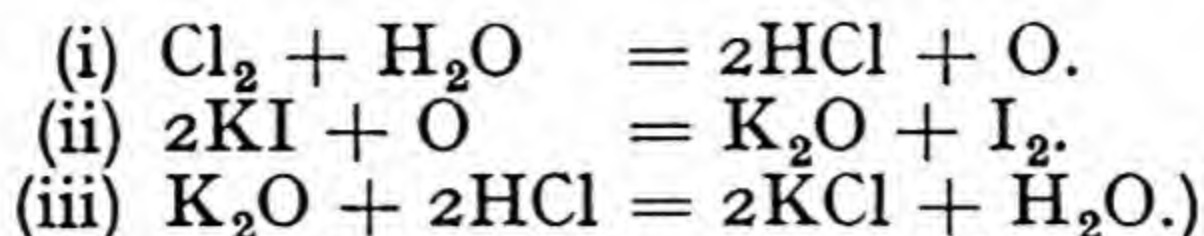
From the above equation it is seen that 1 litre of 0·1N. iodine solution is equivalent to 3·55 grams of chlorine.

Method. The mixture is then diluted to a convenient volume, and aliquot portions are titrated with 0·1N.$Na_2S_2O_3$ solution, using starch as the indicator in the usual way.

For example, in an experiment, 100 c.c. of the chlorine water were allowed to react with about 8 grams of KI dissolved in a small quantity of water, and the mixture was then diluted to 250 c.c. 25 c.c. of this solution required, as a mean of three titrations, 16·5 c.c. of 0·1N.$Na_2S_2O_3$ for the complete reduction of the liberated iodine.

Then, 250 c.c. of the solution would require 165 c.c. of 0·1N.$Na_2S_2O_3$, which are equivalent to 165 c.c. of 0·1N. iodine solution.

Now, 1 litre of 0·1N. iodine is equivalent to 3·55 grams of Cl; therefore, 165 c.c. of 0·1N. iodine are equivalent to 3·55 × 0·165, or 0·586 gram, of Cl. And, since this amount of chlorine was contained in 100 c.c. of solution, the strength of the solution is *5·86 grams of chlorine per litre.*

66. THE ESTIMATION OF BROMINE IN BROMINE WATER. The method of procedure is exactly the same as in the determination of chlorine in chlorine water. A measured volume of the bromine water is added to an excess of KI dissolved in a little water, and the mixture is diluted to a convenient volume. Aliquot portions of this solution are then titrated with 0·1N.$Na_2S_2O_3$ solution in order to estimate the liberated iodine, and the amount is calculated from the titration values. The reaction may be represented by the equation (though here, too, the water plays an intermediate part) :

$$2KI + Br_2 = 2KBr + I_2,$$
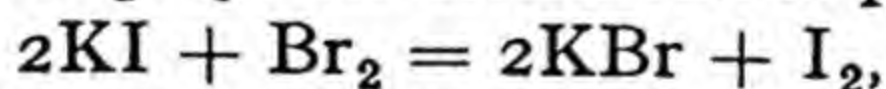
from which it is found that 1 litre of 0·1N. iodine is equivalent to 8·0 grams of bromine.

67. THE DETERMINATION OF HYPOCHLORITES. Hypochlorous acid in the presence of dilute HCl (or acetic acid) oxidizes KI to free iodine according to the equation :

$$HClO + 2KI + HCl = 2KCl + H_2O + I_2$$

(or,

$$HClO + 2KI + CH_3COOH = KCl + CH_3COOK + H_2O + I_2).$$
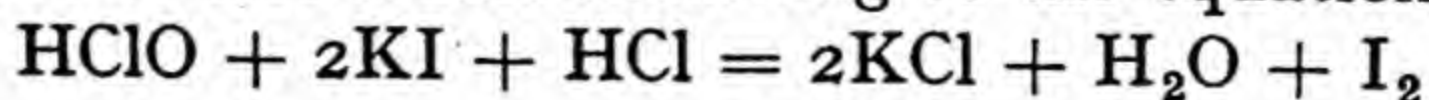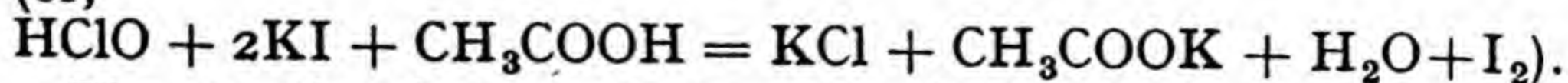
The reaction is immediate, and, therefore, in estimating a

hypochlorite, a known weight of the salt is added to a solution containing excess of KI ; the mixture is then acidified with dilute HCl (or acetic acid) and aliquot portions are titrated with standard sodium thiosulphate, using starch as the indicator. The liberated iodine is thus determined, and the amount of hypochlorite calculated from the titration values : e.g.

To Estimate Potassium Hypochlorite in Aqueous Solution. Aliquot portions of the solution are allowed to react with an excess of potassium iodide, acidified with dilute HCl or acetic acid, and the liberated iodine titrated with $0.1N.Na_2S_2O_3$ solution. The amount of hypochlorite is then determined from the equivalents :

$$I_2 \equiv KClO.$$
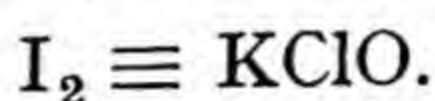
Thus, 254 grams of iodine are equivalent to 90.5 grams of KClO ; i.e. 1 litre of $0.1N.$ iodine is equivalent to 4.525 grams of KClO.

68. THE ESTIMATION OF THE AVAILABLE CHLORINE IN BLEACHING POWDER. When bleaching powder is acted upon with dilute acids chlorine is evolved, and the substance from which the chlorine is evolved may be represented by the formula $Ca(OCl)Cl$. The reactions with acids take place according to the equations :

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2,$$

or $\quad Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$
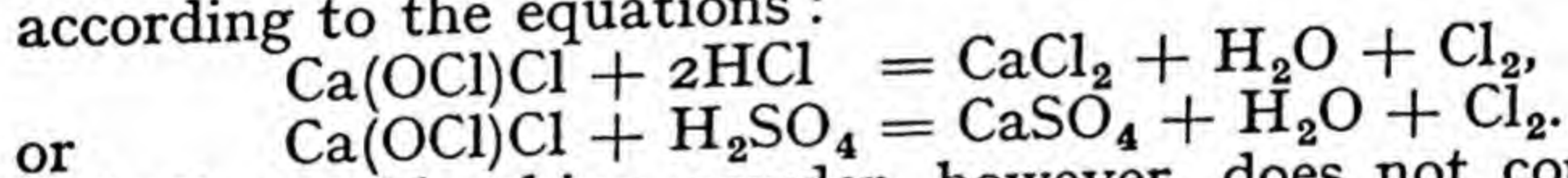
Ordinary bleaching powder, however, does not consist of pure $Ca(OCl)Cl$ alone, but is mixed with some calcium hydroxide (unattacked by the chlorine in the preparation of the bleaching powder) and other chlorinated compounds of calcium such as calcium hypochlorite, $Ca(OCl)_2$, and calcium chlorate, $Ca(ClO_3)_2$. The ' available chlorine ' is that which is liberated from the $Ca(OCl)Cl$ by the action of acids, and its estimation is, thus, of great importance in determining the quality of the bleaching powder. The purest forms of bleaching powder seldom contain more than 36 per cent of $Ca(OCl)Cl$.

(a) *The Estimation of Bleaching Powder by Means of Potassium Iodide and Standard Sodium Thiosulphate.* About 10 to 15 grams of the bleaching powder are weighed in a small mortar and triturated with a little water until a cream-like paste is obtained. The mixture is then diluted to a convenient volume (say 1 litre) and well shaken. Aliquot portions (25 c.c.) of the solution are then transferred to a small flask and a few crystals of KI added (about 2 grams will be enough). The solution is acidified with acetic acid (in

this case a mineral acid cannot be used, as chlorine might thereby be liberated from the calcium chlorate present as an impurity). The acetic acid liberates chlorine from the Ca(OCl)Cl, and an equivalent amount of free iodine is displaced from the KI, viz. :

(i) $Ca(OCl)Cl + 2CH_3COOH = (CH_3COO)_2Ca + Cl_2 + H_2O$,

(ii) $Cl_2 + 2KI = 2KCl + I_2$.
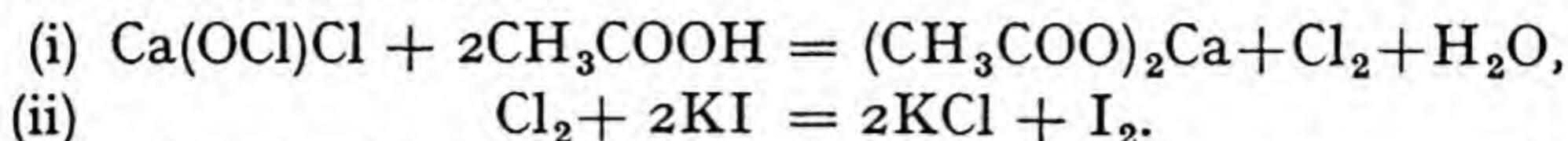
The liberated iodine is then determined by titration with $0.1N.Na_2S_2O_3$, using starch solution as the indicator in the usual way. Three concordant results are obtained, and the amount of chlorine in the bleaching powder is determined from the titration values and expressed as a percentage.

For example, in a determination, 11·50 grams of bleaching powder were triturated with a small quantity of water and diluted to 1 litre. It was found that 25 c.c. of this solution, after treatment with excess of KI and acetic acid, required a mean volume of 26·8 c.c. of $0.1N.Na_2S_2O_3$ to reduce the liberated iodine.

Therefore, 1 litre of the solution would be equivalent to 40×26.8, or 1072 c.c., of $0.1N.Na_2S_2O_3$, which are equivalent to the same volume of 0·1N. iodine.

Now, 1 litre of 0·1N. iodine is equivalent to 3·55 grams of chlorine. Therefore, 1·072 litres of 0·1N. iodine are equivalent to 3.55×1.072, or 3·81 grams, of chlorine.

Thus, the percentage of Ca(OCl)Cl in the bleaching powder is

$$\frac{3.81}{11.50} \times 100, \text{ or } 33\%.$$

(b) *An Alternative Method of Determining the Available Chlorine in Bleaching Powder, by Means of Standard Arsenite Solution and Standard Iodine.* The ' available chlorine ' in bleaching powder may also be determined by means of a standard alkaline solution of As_4O_6. The reaction takes place according to the equation :

$$4Ca(OCl)Cl + As_4O_6 = 2As_2O_5 + 4CaCl_2.$$
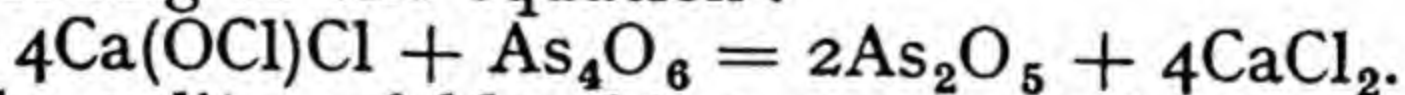
Method. 1 litre of bleaching powder solution is prepared as in (a). Aliquot portions of this solution are then allowed to react with a measured excess of decinormal arsenite solution. The excess arsenite is titrated with decinormal iodine, using starch as the indicator, and the amount of arsenite which has reacted with the Ca(OCl)Cl is determined by difference. Three concordant results are obtained and the available chlorine is then obtained from the titration values, employing the equivalents :

1 litre of o·1N. iodine $\equiv$ 1 litre o·1N.As$_4$O$_6$ $\equiv$ 3·55 grams of chlorine.

[For the method of titrating As$_4$O$_6$ with o·1N. iodine see § 59 (b)].

69. THE DETERMINATION OF IODATES. (a) The general method of determining iodates is based upon the following reaction between hydriodic and iodic acids in the presence of dilute sulphuric acid :

$$HIO_3 + 5HI \rightleftharpoons 3I_2 + 3H_2O.$$
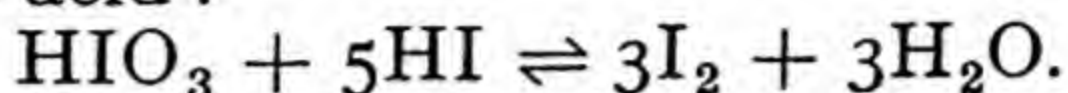
In the reaction of potassium iodate with potassium iodide in the presence of sulphuric acid, the reaction would be :

$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O.$$
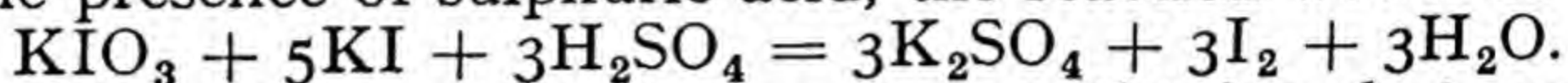
The liberation of the iodine is quantitative, but, as the reaction is rather slow, sufficient time must be allowed for the liberation of iodine to be completed. The free iodine is then titrated with o·1N.Na$_2$S$_2$O$_3$ solution in the usual manner, and the amount of iodate is determined from the equivalents :

$$3I_2 \equiv KIO_3 \; ; \; e.g.$$
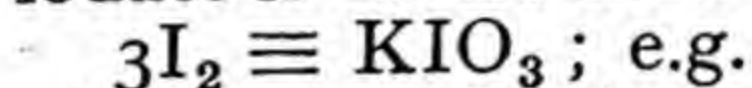
To Determine the Percentage Purity of a Sample of Sodium Iodate. 3·164 grams of the iodate were dissolved in water and diluted to 1 litre. 25 c.c. of this solution required, after treatment with excess of KI and dilute H$_2$SO$_4$, 23·5 c.c. of o·1N.Na$_2$S$_2$O$_3$ solution to reduce the liberated iodine.

Thus, 1 litre of the solution would require 40 × 23·5, or 940 c.c., of o·1N.Na$_2$S$_2$O$_3$, which are equivalent to the same volume of o·1N. iodine.

Now, $$3I_2 \equiv NaIO_3,$$

i.e. 127 grams of iodine, are equivalent to 33·0 grams of NaIO$_3$, so that 1 litre of o·1N. iodine is equivalent to 3·30 grams of NaIO$_3$.

Therefore, 940 c.c. of o·1N. iodine are equivalent to 0·94 × 3·30, or 3·102 grams, of NaIO$_3$.

Thus, the percentage of NaIO$_3$ in the sample of sodium iodate is

$$\frac{3·102}{3·164} \times 100, \text{ or } 98·0\%.$$

(b) *Alternative Method for the Determination of Iodates.* An alternative method for the determination of an iodate consists in absorbing the iodine liberated in the reaction of the iodate with KI and H$_2$SO$_4$ in a known excess of o·1N. arsenite solution, and then titrating the excess with standard iodine as described in § 59 (b). The amount of arsenite oxidized by the liberated iodine can then be determined by

difference. The $NaIO_3$ is estimated from the titration values employing the equivalents :

$$3I_2 \equiv NaIO_3.$$
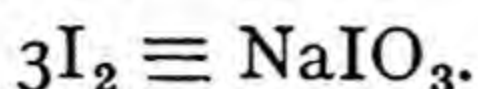
70. THE DETERMINATION OF BROMATES. (a) If dilute sulphuric acid be added to a mixture of a bromate and excess of KI, the bromic acid (formed from the bromate) and the hydriodic acid (formed from the iodide) react to form free iodine according to the equation :

$$HBrO_3 + 6HI = HBr + 3H_2O + 3I_2.$$
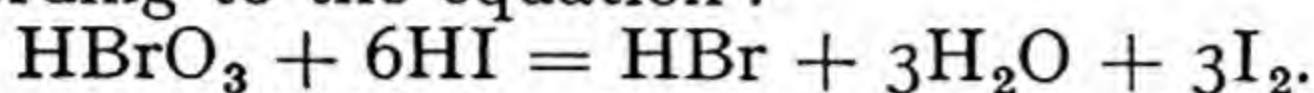
The various stages of the reaction, when potassium bromate is employed, may be represented by the equations :

(i) $2KBrO_3 + H_2SO_4 = K_2SO_4 + 2HBrO_3$.

(ii) $12KI + 6H_2SO_4 = 6K_2SO_4 + 12HI$.

(iii) $2HBrO_3 + 12HI = 2HBr + 6I_2 + 6H_2O$.

The complete reaction may be represented, therefore, by the equation :

$$2KBrO_3 + 12KI + 7H_2SO_4 = 7K_2SO_4 + 2HBr + 6H_2O + 6I_2.$$
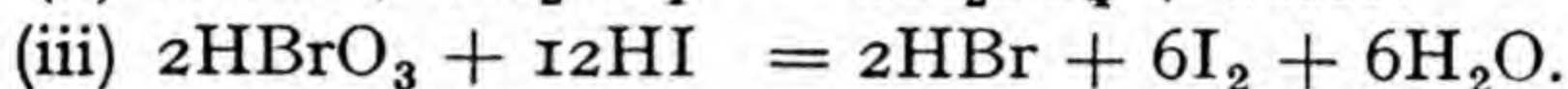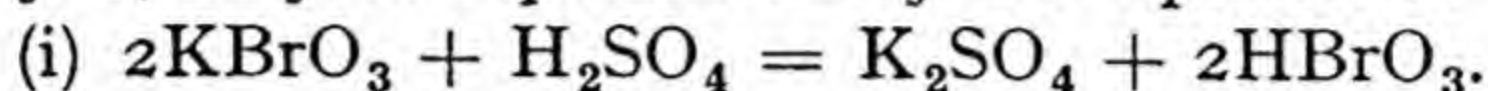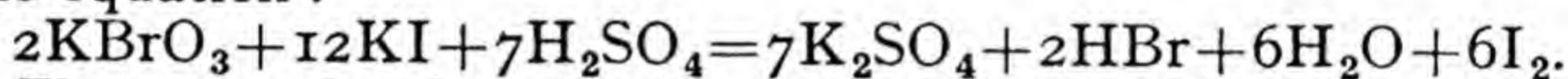
Thus, 3 molecules of iodine are equivalent to 1 molecule of $KBrO_3$; i.e. 1 litre of 0·1N. iodine is equivalent to 2·783 grams of $KBrO_3$.

For example, in an experiment to determine the percentage purity of a sample of potassium bromate, 3·120 grams of the salt were dissolved in water and diluted to 1 litre. 25 c.c. of this solution were treated with excess of KI and dilute H_2SO_4, and, as a mean of three titrations, 27·3 c.c. of 0·1N.$Na_2S_2O_3$ were required to reduce the liberated iodine.

Therefore, 1 litre of the solution would require 40 × 27·3, or 1092 c.c., of 0·1N. thiosulphate to reduce the liberated iodine.

Now, since 1 litre of 0·1N.$Na_2S_2O_3$ is equivalent to 1 litre of 0·1N. iodine, it follows that 1 litre of 0·1N.$Na_2S_2O_3$ is equivalent to 2·783 grams of $KBrO_3$. Therefore 1·092 litres of 0·1N.$Na_2S_2O_3$ are equivalent to 2·783 × 1·092, or 2·940 grams, of $KBrO_3$.

Thus, the percentage of $KBrO_3$ in the potassium bromate is

$$\frac{2·940}{3·120} \times 100, \text{ or } 94·2\%.$$

(b) *An Alternative Method for the Determination of Bromates.* As in the case of an iodate, the bromate may be estimated by means of standard arsenite solution. The bromate solution is acidified with dilute H_2SO_4 and an excess of decinormal arsenite solution added. The bromic acid, formed by the

7

action of the H_2SO_4 on the bromate, oxidizes the arsenite to the arsenate according to the equation :

$$HBrO_3 + 3Na_3AsO_3 = HBr + 3Na_3AsO_4.$$
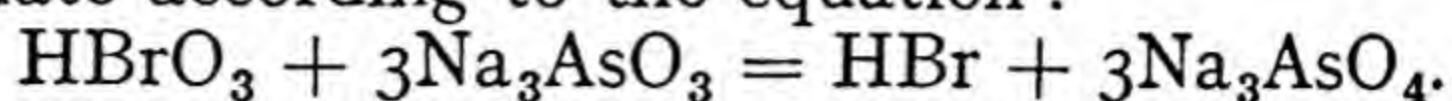
The excess arsenite is then determined by titration with o·1N. iodine (see § 59 (b)), and the amount of arsenite used in reducing the liberated iodine is determined by difference. As before, the amount of bromate is determined from the titration values employing the equivalents :

$$3I_2 \equiv KBrO_3 \text{ (in the case of potassium bromate).}$$
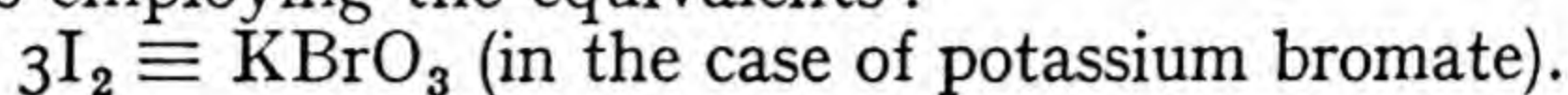
The determination (by the same process as that for bromates and iodates) of CHLORATES does not give satisfactory results owing to the complications due to the liberation of chlorine dioxide from the chlorate by the sulphuric acid. It is true that, employing a dilute solution of a chlorate, approximate results may be obtained by allowing the solution to react with excess of KI in the presence of a moderate excess of dilute H_2SO_4, but it is preferable to carry out the determination in the manner described in § 92 ; i.e. by decomposing the chlorate by heat, and estimating the residual chloride by means of standard silver nitrate solution ; or by the $SnCl_2$ and iodine method described in § 80.

71. THE DETERMINATION OF CHROMATES. The estimation of chromates is based upon the fact that chromic acid, in the presence of dilute HCl, will oxidize potassium iodide to free iodine, the reaction being quantitative. Consequently, a chromate in acid solution will liberate an equivalent amount of iodine from KI according to the equation :

$$2K_2CrO_4 + 16HCl + 6KI = 10KCl + 2CrCl_3 + 8H_2O + 3I_2.$$
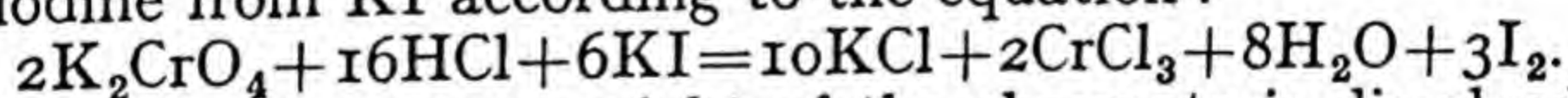
Method. A known weight of the chromate is dissolved in water, excess of dilute HCl is added, and the solution is diluted to a convenient volume ; the dilution should be considerable, so that the green colour of the chromic acid formed in the reaction may not affect the sharpness of the 'end-point' in the subsequent titration. Aliquot portions of the diluted solution are then treated with excess of KI and titrated with o·1N.$Na_2S_2O_3$ in the usual manner, employing starch solution as the indicator. The chromate (in the case of potassium chromate) is then determined from the titration values, employing the equivalents :

$$3I_2 \equiv 2K_2CrO_4.$$
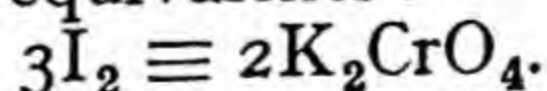
Thus, 127 grams of iodine are equivalent to 64·67 grams of K_2CrO_4 ; i.e. 1 litre of o·1N. iodine is equivalent to 6·467 grams of K_2CrO_4.

For example, in an experiment to determine the percentage purity of a sample of potassium chromate, 1·195 grams of the salt were dissolved in a little water, acidified with dilute HCl, and the solution diluted to 1 litre ; the colour of the solution was then pale enough for titration purposes. Portions of 100 c.c. of the diluted solution were mixed with excess of KI and titrated with 0·1N.$Na_2S_2O_3$, using starch as the indicator. It was found that a mean volume of 18·3 c.c. of 0.1N.$Na_2S_2O_3$ was required to reduce the iodine liberated in each aliquot portion.

Then, 1 litre of the solution would require 183 c.c. of 0·1N.$Na_2S_2O_3$, which is equivalent to the same volume of 0·1N. iodine solution.

Then, since 1 litre of 0·1N. iodine is equivalent to 6·467 grams of K_2CrO_4, 183 c.c. of 0·1N. iodine are equivalent to 6·467 × 0·183, or 1·183 grams, of K_2CrO_4.

Therefore, the percentage of K_2CrO_4 in the potassium chromate is

$$\frac{1·183}{1·195} \times 100, \text{ or } 99\%.$$

Alternative Method for the Determination of Chromates. Chromic acid, in the presence of dilute HCl, will oxidize arsenious oxide to arsenic acid according to the equation :

$$8H_2CrO_4 + 3As_4O_6 = 4Cr_2O_3 + 8H_2O + 6As_2O_5.$$
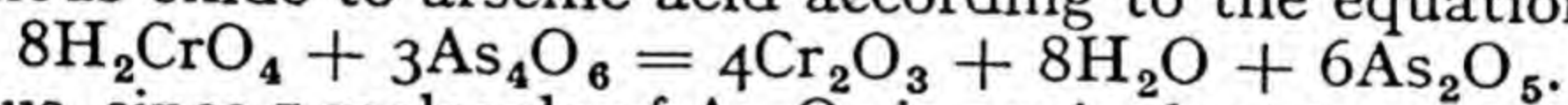
Thus, since 1 molecule of As_4O_6 is equivalent to 4 molecules of iodine, 8 molecules of K_2CrO_4 will be equivalent to 12 molecules of iodine ; i.e.

$$3I_2 \equiv 2K_2CrO_4.$$
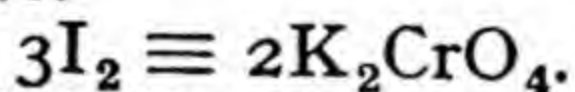
Thus, 1 litre of 0·1N. iodine (12·7 grams) will be equivalent to 6·467 grams of K_2CrO_4.

N.B.—It is essential that, in this method, also, the dilution of the chromate solution must be sufficient to prevent the green colour of the chromic acid obscuring the 'end-point' of the titration with standard iodine.

72. THE DETERMINATION OF PERSULPHATES. We have seen in § 47 that persulphates can be estimated by allowing them to react with a known excess of ferrous sulphate in the presence of dilute sulphuric acid and then determining the excess ferrous iron by means of standard potassium permanganate solution. The persulphates may also be conveniently estimated by allowing them to react with excess of KI in the presence of dilute HCl, and then estimating the liberated iodine by means of standard sodium thiosulphate.

The reactions between the persulphuric acids and hydrogen iodide may be represented by the equations :

   (i) Permonosulphuric acid :
$$H_2SO_5 + 2HI = H_2SO_4 + H_2O + I_2.$$
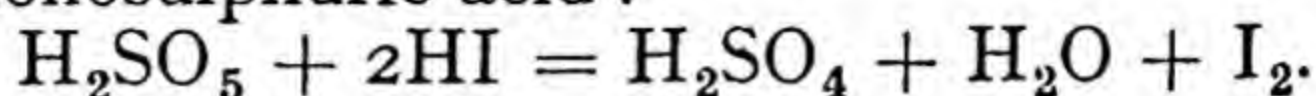
   (ii) Perdisulphuric acid :
$$H_2S_2O_8 + 2HI = 2H_2SO_4 + I_2.$$
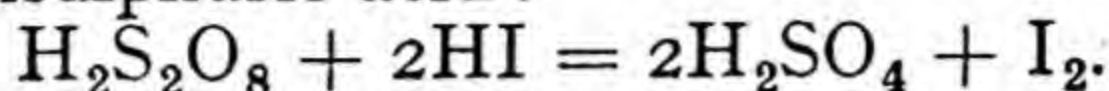
Thus 1 molecule of any persulphate is equivalent to 1 molecule of iodine.

For example, in estimating, by the iodometric method, the amount of sodium perdisulphate in the solution prepared as described in § 47, the procedure was as follows :

100 c.c. of the perdisulphate solution were acidified with dilute HCl and diluted to 250 c.c.   25 c.c. of the solution were transferred to a small flask and an excess of KI solution added. The mixture was then allowed to stand for a short time with frequent shaking, and was then titrated with $0.1N.Na_2S_2O_3$ solution, using starch solution as the indicator.   It was found that, as a mean of three titrations, 13.4 c.c. of $0.1N.Na_2S_2O_3$ were required to reduce the liberated iodine.

Thus, 250 c.c. of the solution are equivalent to 134 c.c. of $0.1N.Na_2S_2O_3$, and also, therefore, to 134 c.c. of $0.1N.$ iodine.

   Now, $I_2 \equiv Na_2S_2O_8$;

i.e. 127 grams of iodine are equivalent to 119 grams of $Na_2S_2O_8$, or 1 litre of $0.1N.$ iodine is equivalent to 11.9 grams of $Na_2S_2O_8$.

Therefore, 134 c.c. of $0.1N.$ iodine are equivalent to 11.9×0.134, or 1.595 gram of $Na_2S_2O_8$.

Thus, 100 c.c. of the original sodium perdisulphate solution contain 1.595 grams of $Na_2S_2O_8$.

Therefore, 1 litre of the perdisulphate contains *15.95 grams of $Na_2S_2O_8$.*

It will be observed that this result compares favourably with that obtained by the permanganate method (see § 47), the difference being less than 0.3%.

73.   THE DETERMINATION OF NITRATES.   The estimation is based upon the fact that a solution of manganous chloride, in strong HCl, decomposes nitric acid quantitatively according to the equation :
$$2HNO_3 + 3MnCl_2 + 6HCl = 3MnCl_4 + 2NO + 4H_2O.$$
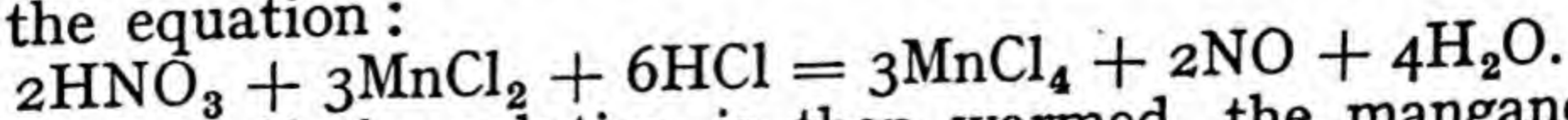
Further, if the solution is then warmed, the manganese tetrachloride, being unstable except at low temperatures, decomposes into the original manganous chloride with the evolution of free chlorine, viz. :
$$3MnCl_4 = 3MnCl_2 + 3Cl_2.$$
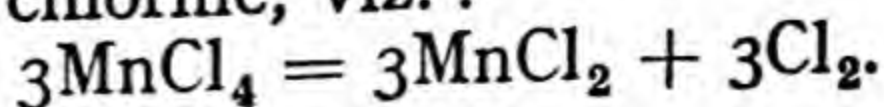
In the case of potassium nitrate, the reaction may be represented, therefore, by the equation :

$$2KNO_3 + 3MnCl_2 + 8HCl = 3MnCl_4 + 2NO + 4H_2O + 2KCl$$
$$\downarrow$$
$$3MnCl_2 + 3Cl_2$$
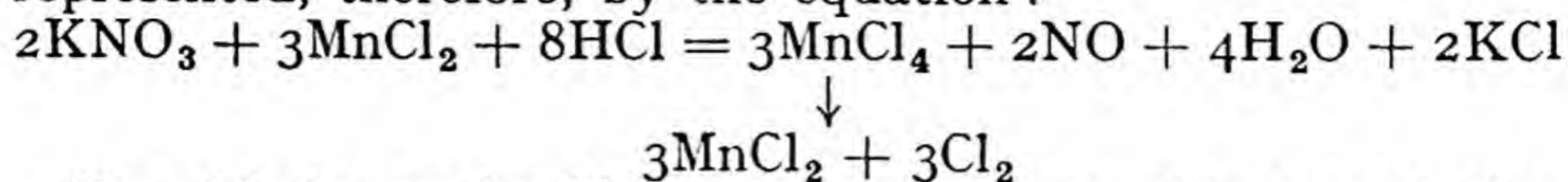
The chlorine evolved in the reaction is passed into a solution of potassium iodide, and an equivalent amount of free iodine is liberated. The iodine is then determined by titration with decinormal sodium thiosulphate solution, using starch as the indicator. The nitrate is then determined from the titration values employing the equivalents (in the case of potassium nitrate) :

$$3I_2 \equiv 3Cl_2 \equiv 2KNO_3 ; \text{ e.g.}$$
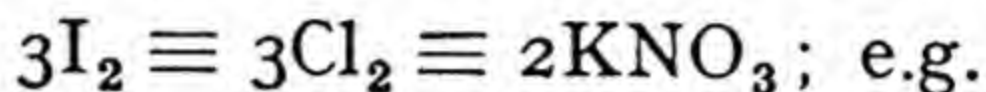
To Estimate the NaNO_3 in Crude Chile Saltpetre. The crude Chile saltpetre is ground to a fine powder and about I gram weighed accurately in a small, round-bottomed flask (preferably one which is fitted with a ground-in stopper and
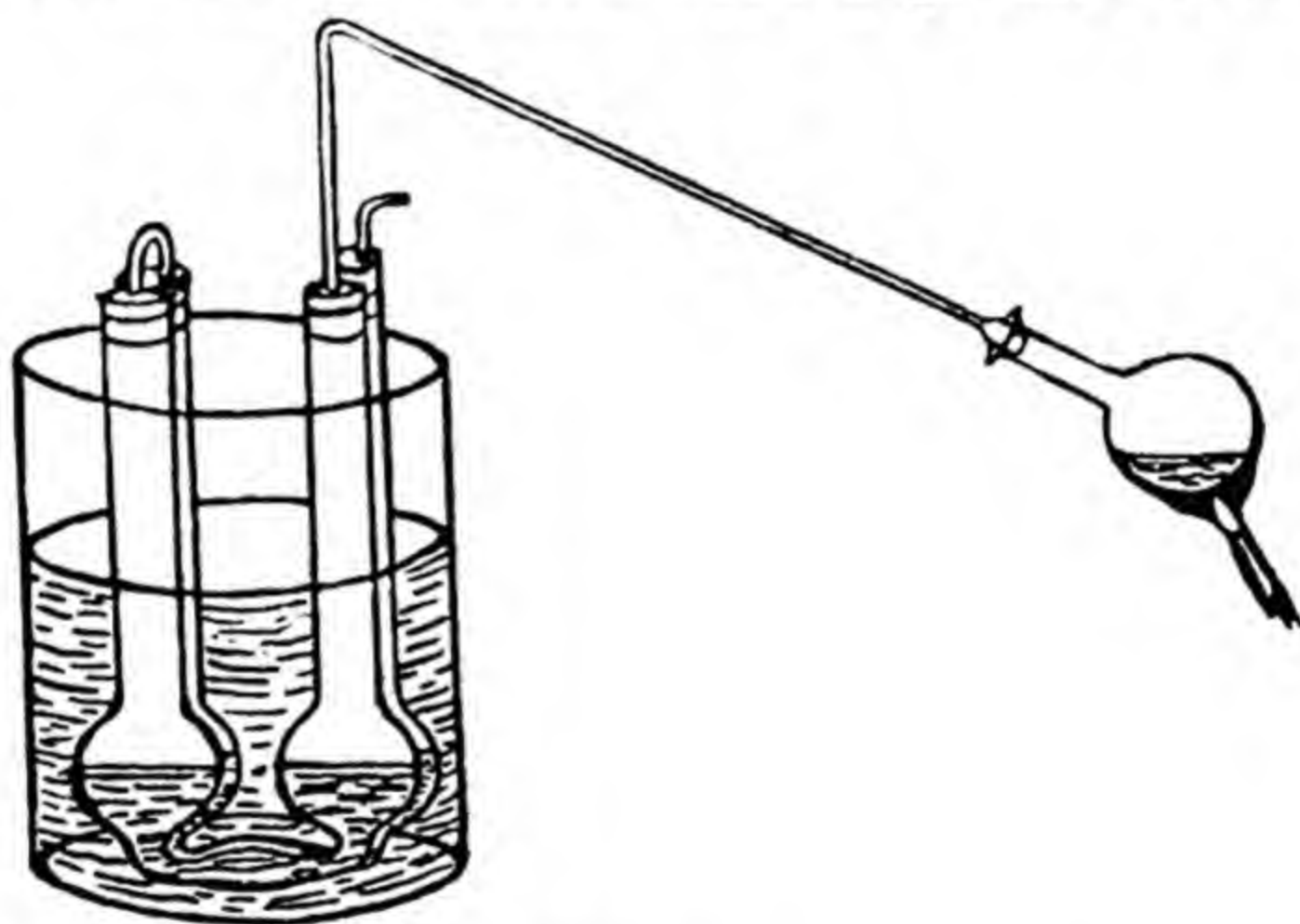
FIG. 4
ESTIMATION OF NITRATES, ETC.

delivery tube). About 8 grams of manganous chloride dissolved in 25 c.c. of strong HCl, and some small pieces of magnesite (magnesium carbonate), are added to the saltpetre in the flask. The flask is connected to two bulbous U-tubes containing about 5 grams of KI dissolved in distilled water (N.B.—The solution should not rise above the widest portions of the bulbs). The U-tubes are connected and immersed in a beaker of cold water, as shown in Fig 4. The flask is then warmed ; a slow stream of chlorine is evolved (the rate of the evolution of the gas being regulated by the amount of heat supplied) ; a current of carbon dioxide is also evolved,

during the reaction, from the magnesite, and this not only helps to drive all the chlorine from the flask but also prevents the KI solution from sucking back into the flask. When the reaction has been completed, the U-tubes are disconnected, allowed to cool to the temperature of the room, if necessary, and their contents washed into a graduated flask (say, 250 c.c.). The solution is then made up to the mark with distilled water, and aliquot portions of the solution thus obtained are titrated with decinormal sodium thiosulphate, using starch as the indicator.

For example, in an experiment, 1·28 grams of the crude saltpetre were treated in the manner described above. When the reaction was complete, the contents of the U-tubes were diluted to 250 c.c., and, as a mean of three titrations, it was found that 25 c.c. of the solution required 27·5 c.c. of 0·1N.$Na_2S_2O_3$ to reduce the liberated iodine.

Thus, 250 c.c. of the solution would require 275 c.c. of 0·1N.$Na_2S_2O_3$.

Now, $$3I_2 \equiv 2NaNO_3.$$

Thus, 127 grams of iodine are equivalent to 28·33 grams of $NaNO_3$; i.e. 1 litre of 0·1N. iodine (equivalent to 1 litre of 0·1N.$Na_2S_2O_3$) is equivalent to 2·833 grams of $NaNO_3$.

Therefore, 275 c.c. of 0·1N. iodine are equivalent to 2·833 × 0·275, or 0·78 gram, of $NaNO_3$.

Thus, the percentage of $NaNO_3$ in crude Chile saltpetre is

$$\frac{0·78}{1·28} \times 100, \text{ or } 61\%.$$

74. THE DETERMINATION OF NITRITES. Nitrites may also be estimated iodometrically, and the method gives more accurate results than are probable when the determination is made with potassium permanganate, as described in § 46. The process is the same as that for nitrates (see § 73), and is based upon the fact that nitrous acid is decomposed by manganous chloride and strong HCl with the evolution of chlorine, when heated. The reaction is expressed by the equations :

(a) $2HNO_2 + MnCl_2 + 2HCl = MnCl_4 + 2H_2O + 2NO.$

(b) $MnCl_4 = MnCl_2 + Cl_2.$
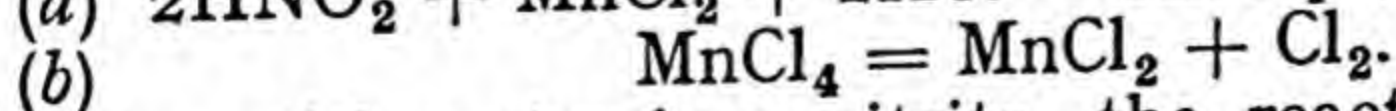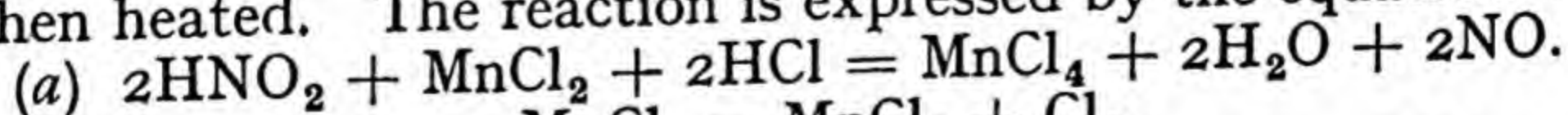
Thus, with potassium nitrite, the reaction would be as follows :

$$2KNO_2 + MnCl_2 + 4HCl = MnCl_4 + 2NO + 2H_2O + 2KCl.$$
$$\downarrow$$
$$MnCl_2 + Cl_2$$

Thus, $$KNO_2 \equiv Cl \equiv I.$$
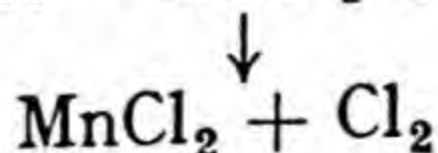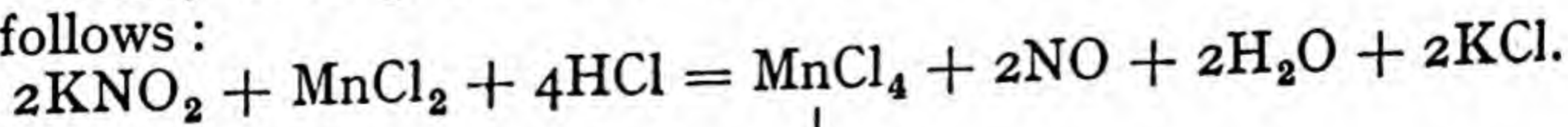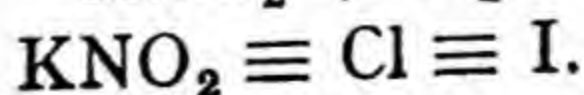
Method. The method of estimation is the same as that for a nitrate (see § 73). The apparatus shown in Fig. 4 is again used, and the same precautions are observed. About 1 gram of the nitrite is weighed accurately into the flask, and a solution of about 8 grams of manganous chloride in concentrated HCl (25 c.c.), and some small pieces of magnesite (see § 73) are added. The chlorine is evolved by gentle heating and absorbed by the solution of potassium iodide (about 5 grams of solid KI are employed) in the U-tubes. When the reaction is completed, the contents of the U-tubes are washed into a 250 c.c. flask and the solution is made up to the mark with distilled water. Aliquot portions of this solution are then titrated with decinormal sodium thiosulphate solution in the usual manner, and the nitrite estimated from the titration values ; e.g.

To Determine the Percentage of KNO$_2$ in Potassium Nitrite Sticks. 1·165 grams of the stick potassium nitrite were taken and treated in the manner described above. After diluting the resulting free iodine solution to 250 c.c., it was found that, as a mean of three titrations, 25 c.c. of the diluted solution required 13·2 c.c. of o·1N.Na$_2$S$_2$O$_3$ to reduce the free iodine to sodium iodide.

Thus, 250 c.c. of the iodine solution would require 132 c.c. of o·1N.Na$_2$S$_2$O$_3$.

Now, $$I \equiv KNO_2$$
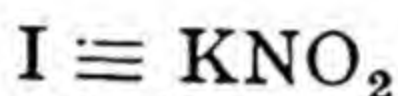
Therefore, 127 grams of iodine are equivalent to 85 grams of KNO$_2$; i.e. 1 litre of o·1N. iodine (which is equivalent to 1 litre of o·1N.Na$_2$S$_2$O$_3$) is equivalent to 8·5 grams of KNO$_2$.

Therefore, 132 c.c. of o·1N. iodine are equivalent to 8·5 × 0·132, or 1·122 grams, of KNO$_2$.

Thus, the percentage of KNO$_2$ in the potassium nitrite sticks is :

$$\frac{1·122}{1·165} \times 100, \text{ or } 96·3\%.$$

N.B.—This method of estimating a nitrite has the great advantage over the permanganate method (see § 46) that the liberation of nitric oxide in the reaction does not affect the accuracy of the determination.

75. THE DETERMINATION OF MANGANESE DIOXIDE. Manganese dioxide may be estimated iodometrically by heating it with strong HCl and absorbing the evolved chlorine in potassium iodide solution. The equivalent amount of liberated iodine is then determined by titration with decinormal sodium thiosulphate solution, and the manganese

dioxide calculated from the titration values. The reactions occurring in the determination are as follow :

(a) $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$
(b) $Cl_2 + 2KI = 2KCl + I_2.$
Thus, $I_2 \equiv Cl_2 \equiv MnO_2.$
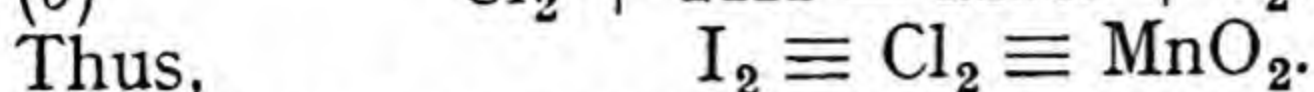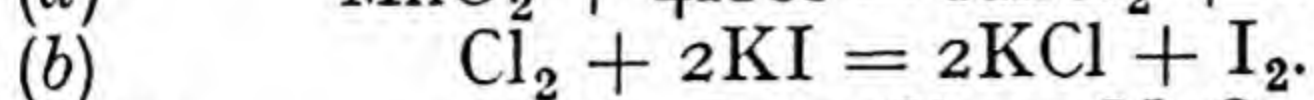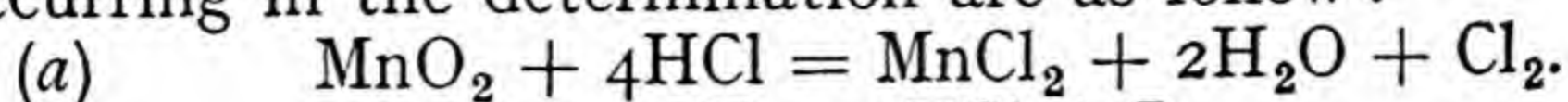
Therefore, 127 grams of iodine are equivalent to 43·5 grams of MnO_2 ; i.e 1 litre of 0·1N. iodine is equivalent to 4·35 grams of MnO_2.

Method. The apparatus and the method of procedure are again exactly the same as in the case of the determination of a nitrate (see § 73) ; e.g.

To Estimate the Available Oxygen in Pyrolusite. The apparatus is assembled as in Fig. 4. About 0·5 gram of the finely powdered ore is weighed accurately into the flask, and a solution of about 5 grams of potassium iodide in water is placed in the U-tubes A few grams of magnesite are then introduced into the flask and about 25 c.c. of strong HCl added. The flask is then connected to the U-tubes and gently heated. The evolution of carbon dioxide from the magnesite not only sweeps out all the chlorine from the flask but also prevents the liquid in the U-tubes from sucking back into the flask. When all the chlorine has been evolved, the contents of the U-tubes are washed into a graduated flask and diluted to a suitable volume. Aliquot portions of this solution are then titrated with decinormal sodium thiosulphate to determine the amount of iodine liberated by the evolved chlorine, and the amount of MnO_2 is determined from the titration values.

For example, 0·472 gram of the pyrolusite was treated as described above and the resulting solution diluted to 250 c.c. 50 c.c. of the diluted solution required, as a mean of three titrations, 20·2 c.c. of 0·1N.$Na_2S_2O_3$ to reduce the liberated iodine to sodium iodide.

Therefore, 250 c.c. of the solution would require 20·2 × 5, or 101 c.c., of 0·1N.$Na_2S_2O_3$, and this volume is equivalent to 101 c.c. of 0·1N. iodine.

Now, 1 litre of 0·1N. iodine is equivalent to 0·8 gram of oxygen.

Therefore 101 c.c. of 0·1N. iodine are equivalent to 0·8 × 0·101, or 0·0808 gram, of oxygen.

Thus the percentage of ' available oxygen ' in the pyrolusite is :

$$\frac{0·0808}{0·472} \times 100, \text{ or } 19·0\%.$$

The result may also be expressed as the percentage of pure MnO_2 in the pyrolusite.

Thus, since 1 litre of 0.1N. iodine is equivalent to 4.35 grams of MnO_2, 101 c.c. of 0.1N. iodine are equivalent to 4.35×0.101, or 0.439 gram, of MnO_2.

Thus, the percentage of MnO_2 in the pyrolusite is

$$\frac{0.439}{0.472} \times 100, \text{ or } 93.0\%.$$

76. THE ESTIMATION OF MANGANESE SESQUIOXIDE. Manganese may also be estimated iodometrically in exactly the same manner as the peroxide. In this case the reaction will be represented by the equation :

$$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + Cl_2.$$
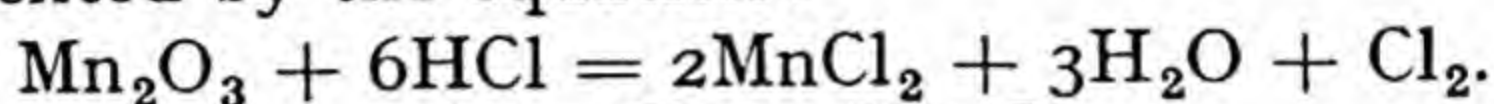
Here, $I_2 \equiv Cl_2 \equiv Mn_2O_3.$

Therefore, 127 grams of iodine are equivalent to 79 grams of Mn_2O_3 ; i.e. 1 litre of 0.1N. iodine is equivalent to 7.9 grams of Mn_2O_3.

The experimental procedure is exactly the same as in the determination of the manganese peroxide (see § 75), and the sesquioxide is estimated from the titration values employing the above equivalents.

77. THE DETERMINATION OF HYDROGEN PEROXIDE. Hydrogen peroxide, in the presence of dilute sulphuric acid, oxidizes potassium iodide to free iodine according to the equation :

$$H_2O_2 + 2KI + H_2SO_4 = K_2SO_4 + 2H_2O + I_2.$$
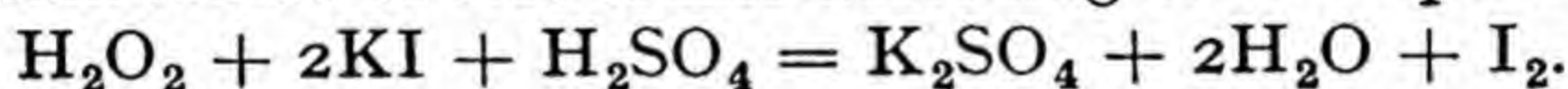
Method. The hydrogen peroxide solution is diluted to a convenient volume, if necessary, and aliquot portions are acidified with dilute sulphuric acid and treated with excess of KI. The liberated iodine is then titrated with decinormal sodium thiosulphate solution, using starch solution as the indicator. The strength of the peroxide solution is then determined from the titration values employing the equivalents : $I_2 \equiv H_2O_2.$
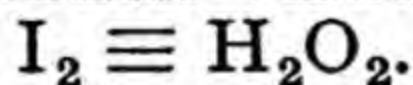
Thus, 127 grams of iodine are equivalent to 17 grams of H_2O_2 ; i.e. 1 litre of 0.1N. iodine is equivalent to 1.7 grams of H_2O_2.

For example, portions of 25 c.c. of a hydrogen peroxide solution were diluted to 250 c.c., and aliquot portions were acidified with dilute H_2SO_4 and treated with excess of KI solution. As a mean of three titrations, it was found that 18.4 c.c. of 0.1N.$Na_2S_2O_3$ were required to reduce the liberated iodine in 25 c.c. of the diluted solution.

Therefore, 250 c.c. of the diluted solution are equivalent to 184 c.c. of $0.1N.Na_2S_2O_3$, and also, therefore, to 184 c.c. of $0.1N$. iodine.

Thus, 25 c.c. of the *original* solution are equivalent to 184 c.c. of $0.1N$. iodine ; i.e. 1 litre of the original solution is equivalent to 184×40, or 7360 c.c. of $0.1N$. iodine.

Now, 1 litre of $0.1N$. iodine is equivalent to 1·7 grams of H_2O_2. Therefore, 7·36 litres of $0.1N$. iodine are equivalent to 1.7×7.36, or 12·5 grams, of H_2O_2.

Thus, the hydrogen peroxide solution contains *12·5 grams of H_2O_2 per litre.*

78. THE DETERMINATION OF VANADIUM COMPOUNDS. Any of the various vanadates—meta-vanadates, ortho-vanadates, pyro-vanadates, and other complex vanadates—may be estimated indirectly by a iodometric method. The determination is based upon the fact that vanadic anhydride, V_2O_5, is reduced to vanadium tetroxide when heated with potassium bromide and strong HCl. The actual reduction is effected by the hydrobromic acid formed in the reaction between the bromide and the HCl. The reaction may be represented, therefore, by the equation :
$$V_2O_5 + 2HBr = V_2O_4 + H_2O + Br_2.$$
The evolved bromine vapour is absorbed in KI solution and an equivalent amount of iodine is liberated, viz :
$$2KI + Br_2 = 2KBr + I_2.$$
The free iodine is then determined by means of standard sodium thiosulphate and the vanadate estimated, in terms of V_2O_5, from the titration values employing the equivalents :
$$V_2O_5 \equiv Br_2 \equiv I_2.$$
Thus, 127 grams of iodine are equivalent to 91 grams of V_2O_5 ; i.e. 1 litre of $0.1N$. iodine is equivalent to 9·1 grams of V_2O_5 ; e.g.
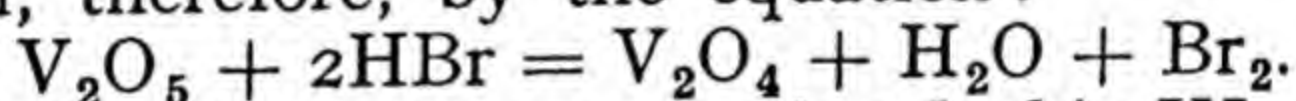
To Determine a Vanadate. The apparatus used is again the same as in the determination of nitrates (see § 73, Fig. 4). About 0·5 gram of the finely powdered vanadate is introduced into the flask, and about 2 grams of KBr and 30 c.c. of strong HCl, together with a few pieces of magnesite, are added. The object of the magnesite is to provide a steady stream of carbon dioxide to sweep all the bromine vapour out of the flask, and also to prevent the liquid in the U-tubes sucking back into the flask. The flask is connected to the U-tubes, which contain about 4 grams of KI dissolved in water. The contents of the flask are then boiled until the liquid is clear

blue in colour ; this shows that the reduction of the vanadate to V_2O_4 is complete.

The bromine vapour liberates an equivalent amount of iodine from the KI solution, and, when the reaction is ended, the contents of the U-tubes are washed into a graduated flask and diluted to a suitable volume. Aliquot portions of this solution are then titrated with decinormal sodium thiosulphate in the usual manner, and the amount of V_2O_5 is then calculated.

N.B.—In some cases it may be found more convenient to titrate the free iodine with centinormal sodium thiosulphate solution.

OTHER IODOMETRIC DETERMINATIONS

79. THE ESTIMATION OF TIN AS STANNOUS CHLORIDE. Pure stannous chloride, in the presence of HCl, will reduce free iodine to hydrogen iodide, and is itself oxidized to stannic chloride according to the equation :

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$
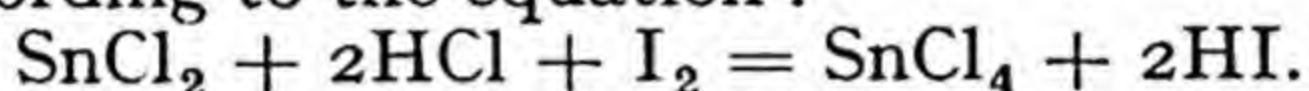
It is supposed that stannic chlor-iodide, $SnCl_2I_2$, is first formed, and that this is then decomposed by the HCl into stannic chloride and hydrogen iodide, viz. :

$$SnCl_2I_2 + 2HCl = SnCl_4 + 2HI.$$
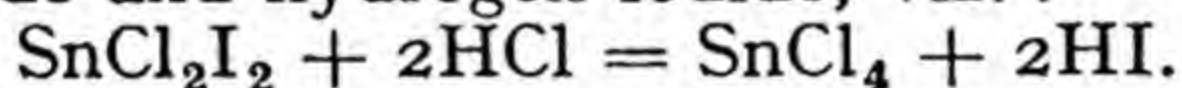
It is upon this reaction that the estimation of tin is based, and the method is of great use in estimating the tin in tin ores and alloys, though *it cannot be employed if lead is present in the alloy*, since the ' end-point ' of the titration would be obscured by the precipitation of yellow lead iodide by the intermediate product—stannic chlor-iodide ; e.g. :

To Determine the Percentage of Tin in an Alloy. An accurately known weight of the alloy is dissolved in dilute HCl, cooled, and diluted to a convenient volume. Aliquot portions of this solution are then titrated directly with decinormal iodine solution, using starch as the indicator ; or, alternatively, excess of decinormal iodine may be added to the solution and the excess iodine determined by titration with decinormal sodium thiosulphate. Three concordant results are obtained, and the percentage of tin in the alloy calculated from the titration values using the equivalents :

$$I_2 = Sn.$$
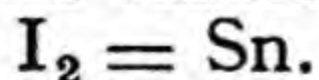
Thus, 127 grams of iodine are equivalent to 59·5 grams of Sn ; i.e. 1 litre of 0·1N. iodine is equivalent to 5·95 grams of Sn.

For example, in an experiment, 3·013 grams of an alloy were dissolved in dilute HCl and the solution diluted to 250 c.c. As a mean of three titrations, 25 c.c. of the diluted solution required 19·4 c.c. of 0·1N. iodine to effect the blue colour with starch solution.

Therefore, 250 c.c. of the solution would require 194 c.c. of 0·1N. iodine. And, since 1 litre of 0·1N. iodine is equivalent to 5·95 grams of Sn, 194 c.c. of 0·1N. iodine will be equivalent to 5·95 × 0·194, or 1·154 grams, of Sn.

Therefore, the alloy contains $\dfrac{1·154}{3·013} \times 100$, or *38·3%, of tin.*

80. THE ESTIMATION OF CHLORATES BY MEANS OF STANNOUS CHLORIDE AND STANDARD IODINE. Pure stannous chloride, in the presence of HCl, is oxidized by a chlorate to stannic chloride, viz. :

$$KClO_3 + 6HCl + 3SnCl_2 = KCl + 3H_2O + 3SnCl_4.$$
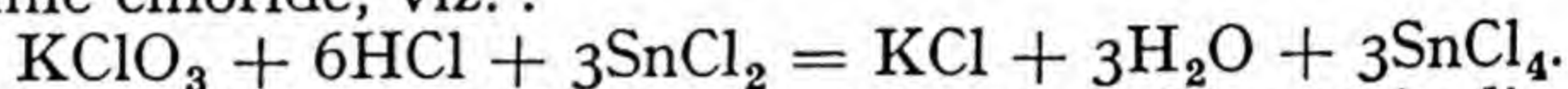
Consequently, if a known weight of a chlorate is digested with a known excess of stannous chloride dissolved in dilute HCl, and the excess $SnCl_2$ determined by titration with standard iodine solution (see § 79), then the amount of chlorate can be determined from the titration values.

To Prepare the Standard Solution of Stannous Chloride. About 1 gram of pure stannous chloride is weighed accurately, dissolved in dilute HCl, and diluted to 250 c.c. This solution is then standardized by titrating with 0·1N. iodine solution, and the strength of the stannous chloride is expressed in terms of 0·1N. iodine, viz. 1 c.c. is equivalent to ' x ' c.c. of 0·1N. iodine ; e.g.

To Determine the Percentage of KClO₃ in a Mixture of Potassium Chlorate and Chloride. A known quantity of the mixture is dissolved in water and diluted to a convenient volume. Aliquot portions of this solution are then treated with an excess of the standard $SnCl_2$ solution, prepared in the manner described above. The solution is then allowed to stand for about 10 minutes until the reaction is completed. The excess $SnCl_2$ is determined by titration with 0·1N. iodine solution, and the potassium chlorate is estimated from the titration values employing the equivalents :

$$3I_2 \equiv 3SnCl_2 \equiv KClO_3.$$
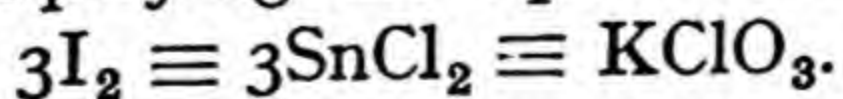
Thus, 127 grams of iodine are equivalent to 20·41 grams of KClO₃ ; i.e. 1 litre of 0·1N. iodine is equivalent to 2·041 grams of KClO₃.

For example, 2·192 grams of the mixture were dissolved in

water and diluted to 250 c.c. 25 c.c. of this solution were then treated with 50 c.c. of a standard solution of $SnCl_2$ (I c.c. of $SnCl_2$ solution $\equiv$ I·I c.c. of 0·IN. iodine).

Thus, the $SnCl_2$ added was equivalent to I·I $\times$ 50, or 55 c.c., of 0·IN. iodine. After standing for about ten minutes the excess $SnCl_2$ was determined by titration with 0·IN. iodine, using starch as the indicator. As a mean of three determinations, 23·8 c.c. of the 0·IN. iodine were required.

Therefore, (50 − 23·8), or 26·2 c.c., of 0·IN. iodine are equivalent to the $KClO_3$ in 25 c.c. of the original solution.

Thus, 250 c.c. of the chlorate solution are equivalent to 262 c.c. of 0·IN. iodine.

Then, since I litre of 0·IN. iodine is equivalent to 2·04I grams of $KClO_3$, 262 c.c. of 0·IN. iodine will be equivalent to 2·04I $\times$ 0·262, or 0·535 gram, of $KClO_3$.

Therefore the percentage of $KClO_3$ in the mixture is

$$\frac{0·535}{2·192} \times 100, \text{ or } 24·4\%.$$

81. The Iodometric Determination of Iron in the Ferric Condition. Iron, in the ferric condition, may be determined by means of potassium iodide and standard sodium thiosulphate solution. For example, ferric chloride, in the presence of HCl, oxidizes potassium iodide to free iodine, according to the equation :

$$2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

This method of determination gives accurate results, but it has the disadvantage that the reaction is extremely slow, especially toward the end, and, where a quick determination is essential, it is preferable to employ the titanous chloride method of determination (see § IOI).

To Determine a Ferric Iron Solution. Suitable aliquot portions of the ferric iron solution are acidified with HCl, and a few crystals of KI added. The solution is then allowed to stand, with occasional shaking, for, at least, half an hour, and is then titrated with 0·IN.$Na_2S_2O_3$ in order to determine the liberated iodine.

For example, it was found that, as a mean of three determinations, 25 c.c. of the ferric iron solution, after reduction with KI, required 18·8 c.c. of 0·IN.$Na_2S_2O_3$ to reduce the liberated iodine.

Therefore, I litre of the ferric iron solution would be equivalent to 40 $\times$ 18·8, or 752 c.c., of 0·IN.$Na_2S_2O_3$, which is equivalent to the same volume of 0·IN. iodine.

Now, $I_2 \equiv 2Fe.$
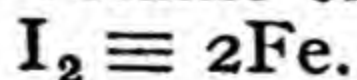
Thus, 127 grams of iodine are equivalent to 56 grams of Fe. Therefore, 1 litre of 0·1N. iodine is equivalent to 5·6 grams of Fe.

Therefore 752 c.c. of 0·1N. iodine are equivalent to 5·6 × 0·752, or 4·21 grams, of Fe.

Thus 1 litre of the solution contains *4·21 grams of iron in the ferric condition.*

82. THE IODOMETRIC DETERMINATION OF COPPER. The estimation is based upon the fact that cupric salts, in the presence of acetic acid (mineral acids render the reaction rather complex), are reduced by potassium iodide to cuprous iodide and free iodine ; e.g. :

$$2CuSO_4 + 4HI = Cu_2I_2 + I_2 + 2H_2SO_4.$$
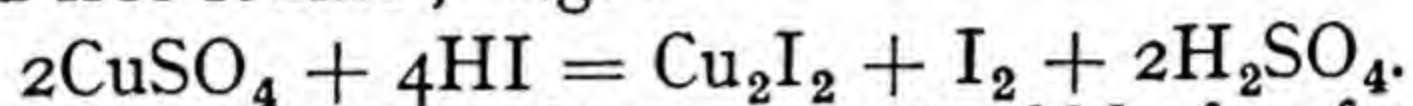
It is essential that the salt solution should be free from mineral acid. Copper sulphate, for example, frequently contains a little free H_2SO_4 in solution, and this must be destroyed by adding dilute Na_2CO_3 solution until a precipitate of basic copper carbonate begins to form. The solution is then acidified with a little acetic acid, and a few crystals of KI are added. Free iodine is thus liberated and is determined by titration with 0·1N.$Na_2S_2O_3$ solution in the usual manner.

N.B.—A little practice is necessary to obtain the ' end-point ' satisfactorily since the precipitated cuprous iodide renders its detection a little difficult. The copper is then determined from the titration values, employing the equivalents :

$$I \equiv Cu.$$
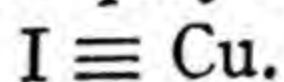
Thus, 127 grams of iodine are equivalent to 63·6 grams of Cu ; i.e. 1 litre of 0·1N. iodine is equivalent to 6·36 grams of Cu.

To Determine the Percentage of Copper in Hydrated Copper Sulphate. 5·247 grams of hydrated copper sulphate were dissolved in water ; dilute Na_2CO_3 solution was added from a pipette until a blue-green precipitate of basic copper carbonate just appeared ; acetic acid was then introduced from a burette, a drop at a time, until the solution was just acid, and a further excess of about 2 c.c. was run in. The solution was then diluted to 250 c.c.

Portions of 25 c.c. of the solution were transferred to small flasks, a few crystals of KI added to each portion, and the liberated iodine titrated with decinormal thiosulphate solution, using starch as the indicator. It was found that, as a mean of three determinations, 25 c.c. of the copper solution required 21·2 c.c. of the 0·1N.$Na_2S_2O_3$ to reduce the free iodine.

Therefore, 250 c.c. of the copper solution would require

212 c.c. of o·1N.Na₂S₂O₃, which are equivalent to the same volume of o·1N. iodine.

Then, since 1 litre of o·1N. iodine is equivalent to 6·36 grams of Cu, 212 c.c. of o·1N. iodine are equivalent to 6·36 × 0·212, or 1·348 grams, of Cu.

Therefore, the percentage of copper in hydrated copper sulphate is :

$$\frac{1\cdot348}{5\cdot247} \times 100, \text{ or } 25\cdot5\%.$$

83. THE IODOMETRIC DETERMINATION OF BASIC HYDROXIDES. Solutions of basic hydroxides (e.g. NaOH, KOH, Ca(OH)₂, Ba(OH)₂, etc.) when allowed to react with free iodine at room temperature give a mixture of a hypoiodite and an iodide, viz. :

$$2KOH + I_2 = KIO + KI + H_2O.$$

But if the reaction takes place at a higher temperature the final products are an iodate and an iodide, viz. :

$$6KOH + 3I_2 = KIO_3 + 5KI + 3H_2O.$$

Thus, by adding a measured excess of standard iodine solution to a basic hydroxide, heating, cooling, and titrating the excess iodine with either standard thiosulphate or standard arsenic solution, the basic hydroxide may be conveniently estimated ; e.g. :

To Determine the Percentage of KOH in a Sample of Commercial Caustic Potash. 1·50 grams of the commercial caustic potash were dissolved in distilled water and diluted to 250 c.c. 25 c.c. of the solution were transferred to a small flask, and 50 c.c. of o·1N. iodine solution added. The solution was then heated gently on a sand tray until boiling commenced ; the solution was allowed to cool, and titrated with o·1N. arsenic solution, excess of NaHCO₃ solution being added to prevent the reversal of the reaction (see § 59 (*b*)).

As a mean of three determinations, it was found that 26·6 c.c. of o·1N. arsenite were required to reduce the excess iodine.

Therefore, (50—26·6), or 23·4 c.c., of o·1N. iodine have been used in oxidizing 25 c.c. of the KOH solution to KIO₃ and KI.

Thus, 250 c.c. of the KOH solution would require 234 c.c. of o·1N. iodine for complete oxidation.

Now, I ≡ KOH.

Thus, 127 grams of iodine are equivalent to 56 grams of KOH. Therefore 1 litre of o·1N. iodine is equivalent to 5·6 grams of KOH.

Therefore, 234 c.c. of 0·1N. iodine are equivalent to 5·6 × 0·234, or 1·31 grams, of KOH.

Thus, the percentage of KOH in the potash is :

$$\frac{1·31}{1·50} \times 100, \text{ or } 87·3\%.$$

84. THE IODOMETRIC DETERMINATION OF THE DEGREE OF HYDROLYSIS OF SALTS OF STRONG ACIDS AND WEAK BASES. Hydrolysis, in the case of inorganic salts, is the reverse of neutralization, and may be expressed generally :

SALT + WATER ⇌ ACID + BASE (hydroxide or basic salt).

We have already seen that the salts of weak acids and strong bases are alkaline in solution as the result of hydrolysis ; e.g. Na_2CO_3, and KCN (see § 9). In an analogous manner, the salts of strong acids and weak bases are acidic to some indicators in aqueous solution. Such salts as aluminium chloride, aluminium sulphate, ferric chloride, ferrous sulphate, cobalt sulphate, nickel sulphate, etc., are partially hydrolyzed in aqueous solution to the free basic hydroxide (or, else, a basic salt) and the free acid.

For example, aluminium chloride is partially hydrolyzed in aqueous solution to the free base (aluminium hydroxide) and the free acid (hydrochloric acid) :

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl ;$$
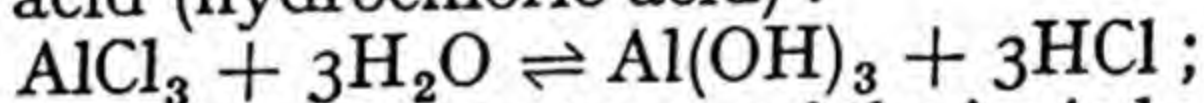
or, expressing the reaction in terms of the ionic hypothesis :

$$AlCl_3 \rightleftharpoons \overset{+++}{Al} + 3\overset{-}{Cl}$$

$$3H_2O \rightleftharpoons 3\overset{-}{OH} + 3\overset{+}{H}$$

$$\Updownarrow$$

$$Al(OH)_3$$
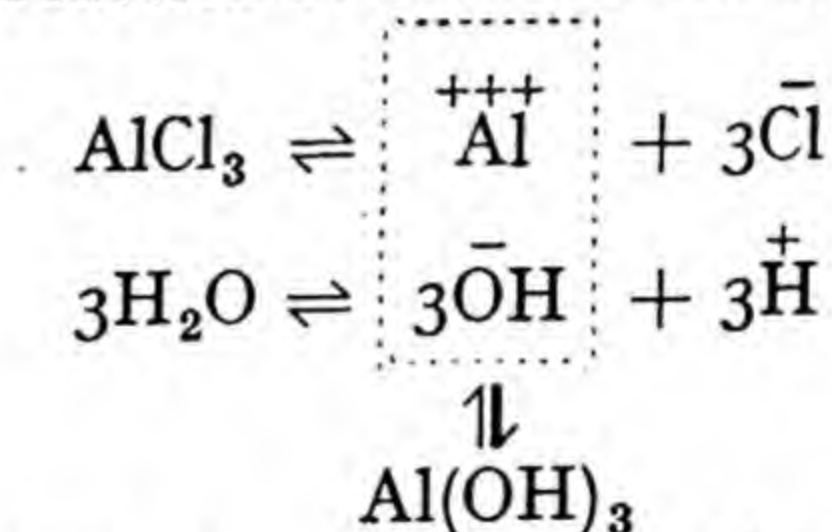
The electro-positive aluminium ions from the solution of salt unite with the electro-negative hydroxyl ions from the water to form the feebly dissociated aluminium hydroxide. In consequence, the excess of hydrogen ions in the solution gives it acid characteristics. Neutralization will then take place between the free base and the free, dissociated acid, and, eventually, *an equilibrium point will be reached when the speed of hydrolysis is equal to the speed of neutralization.*

Aluminium sulphate, in a similar manner, is supposed to be hydrolytically dissociated into the free acid (sulphuric) and a basic salt according to the equation :

$$Al_2(SO_4)_3 + 2H_2O \rightleftharpoons 2AlSO_4(OH) + H_2SO_4.$$
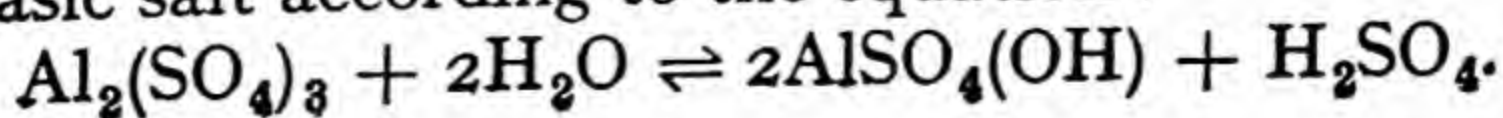
The amount of free acid formed in such a hydrolytic reaction may be estimated by allowing the aqueous solution of the salt to react with an excess of potassium iodide-iodate mixture. Free iodine is liberated from the mixture by the free acid in solution, and the amount of iodine is determined by titration with decinormal sodium thiosulphate in the usual manner.

N.B.—The iodide-iodate mixture is composed of potassium iodide and potassium iodate in the molecular proportions of 5 : 1. It can be readily prepared by boiling a moderately strong solution of KOH with excess of pure, resublimed iodine, viz. :

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$
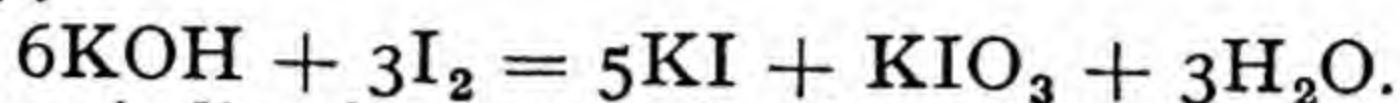
The excess iodine is removed, after the solution has cooled, and the mixture is then ready for use.

It will be seen that the action of free acid on the iodide-iodate mixture reverses the above reaction, and we may, therefore, express the method of estimation in the following general way :

$$3I_2 + 3H_2O \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftharpoons}} 5HI + HIO_3.$$
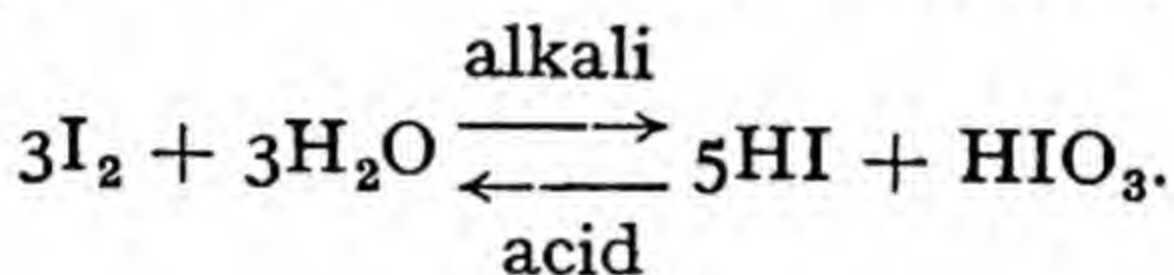
To Determine the Degree of Hydrolysis of a Sixteenth-normal Solution of Aluminium Chloride at Ordinary Temperature. Since *one* molecule of $AlCl_3$ is equivalent to *three* atoms of hydrogen, it follows that a *normal solution* will be a *one-third molar* solution ; therefore a *one-sixteenth normal* solution will be a *one-fortyeighth molar* solution, and will contain $\frac{133 \cdot 5}{48}$, or 2·781 grams, of $AlCl_3$ per litre.

2·781 grams of pure, anhyrous $AlCl_3$ are weighed in a small flask, dissolved in a little water, and diluted to 1 litre.

250 c.c. of this solution are then mixed with excess of the iodide-iodate mixture, and the solution is gently heated for about 15 minutes. The free iodine, liberated from the mixture by the free HCl formed in the hydrolysis of the $AlCl_3$, is then determined by titration with standard $Na_2S_2O_3$ in the usual manner, employing starch as the indicator (in this case it is best to use *centinormal* sodium thiosulphate). The amount of $AlCl_3$ decomposed by hydrolysis is then determined from the titration values employing the equivalents :

$$AlCl_3 \equiv 3HCl \equiv 3I.$$
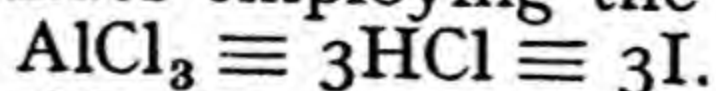
Thus, 127 grams of iodine are equivalent to 44·5 grams of

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$AlCl_3$; i.e. 1 litre of 0·01N. iodine is equivalent to 0·445 gram of $AlCl_3$.

For example, in the above experiment, 250 c.c. of the sixteenth-normal solution of $AlCl_3$ were allowed to react with excess of the iodide-iodate mixture as described above. It was found, as a mean of three determinations, that 21·5 c.c. of 0·01N.$Na_2S_2O_3$ solution were required to reduce the iodine (liberated from the iodide-iodate mixture by the free HCl due to the hydrolysis of the $AlCl_3$).

Thus, 1 litre of the $AlCl_3$ solution will liberate the equivalent of 21·5 × 4, or 86·0 c.c., of 0·01N. iodine.

And since 1 litre of 0·01N. iodine is equivalent to 0·445 gram of $AlCl_3$, 86·0 c.c. of 0·01N. iodine will be equivalent to 0·445 × 0·086, or 0·038 gram, of $AlCl_3$.

Thus, the percentage of $AlCl_3$ hydrolyzed in a sixteenth-normal solution of the salt is :

$$\frac{0·038}{2·781} \times 100, \text{ or } 13·7\%.$$

85. THE IODOMETRIC DETERMINATION OF FORMALDE-HYDE. Formaldehyde, in aqueous solution, will reduce free iodine to sodium iodide, in the presence of sodium hydroxide, according to the equation :

$$H.CHO + I_2 + 3NaOH = H.COONa + 2NaI + 2H_2O.$$
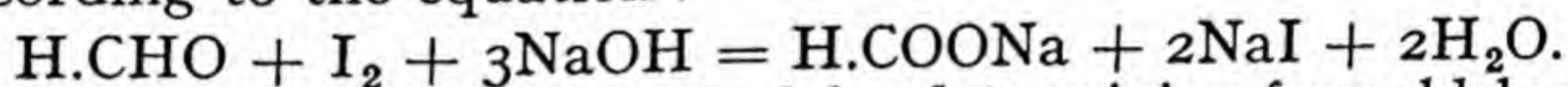
Upon this reaction a method for determining formaldehyde in aqueous solution has been based.

Method. Aliquot portions of the formaldehyde solution are diluted to convenient volumes and a measured excess of standard iodine solution is added to each portion. NaOH is then added to each mixture until the liquid turns yellow, and the mixture is then set aside for about half an hour to allow the reaction to proceed to completion. Dilute HCl is then added to the solution in order to completely liberate the excess iodine as the alkali tends to 'hold' the excess iodine in solution (see the note on the iodide-iodate mixture, § 84). The excess iodine is then determined by titration with 0·1N.$Na_2S_2O_3$ in the usual manner, and the formaldehyde is determined from the titration values employing the equiva-lents : $$I_2 \equiv H.CHO$$
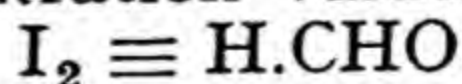
Thus, 127 grams of iodine are equivalent to 15·0 of grams H.CHO ; i.e. 1 litre of 0·1N. iodine is equivalent to 1·50 grams of H.CHO.

For example, 25 c.c. of a formaldehyde solution were diluted to 250 c.c. with distilled water. 50 c.c. of this solution were

then mixed with 50 c.c. of o·1N. iodine solution and treated with NaOH as described above. When the oxidation of the formaldehyde had been completed, and the excess iodine liberated from the NaOH by means of a little HCl, the solution was titrated with o·1N.$Na_2S_2O_3$ solution, 28·4 c.c. of which were needed to reduce the excess iodine to sodium iodide.

Therefore, (50 − 28·4), or 21·6 c.c., of o·1N. iodine have been reduced by the formaldehyde in 50 c.c. of the diluted solution.

Thus, 25 c.c. of the original formaldehyde solution (250 c.c. of diluted solution) would reduce 5 × 21·6, or 108 c.c., of o·1N. iodine to NaI. And 1 litre of o·1N. iodine is equivalent to 1·50 grams of H.CHO. Therefore, 108 c.c. of o·1N. iodine are equivalent to 1·50 × 0·108, or 0·162 gram, of H.CHO.

Thus 1 litre of the formaldehyde solution would contain 40 × 0·162, or *6·48 grams, of H.CHO.*

SUGGESTED EXPERIMENTS ON CHAPTER V

1. Given a decinormal solution of iodine, determine the percentage purity of samples of (a) sodium arsenite, and (b) sodium arsenate.

2. Determine the percentage of antimony in tartar emetic given a decinormal solution of iodine.

3. You are provided with 250 c.c. of normal NaOH. Warm the solution and pass in sulphur dioxide for about ten minutes, and cool. By means of decinormal solutions of iodine and sodium thiosulphate determine the percentage of NaOH which has been converted to sodium sulphite.

4. By means of potassium iodide and decinormal sodium thiosulphate determine the strength of a given solution of sodium hypochlorite.

5. Given solid KI and a decinormal solution of sodium thiosulphate, determine (a) the percentage of Ca(OCl)Cl in the laboratory bleaching powder, (b) the strength of the laboratory bromine water in grams per c.c.

6. You are provided with solid KI and decinormal sodium thiosulphate. Determine the percentage purity of (a) potassium iodate, (b) potassium bromate, and (c) potassium chromate.

7. Repeat experiment 6, using an alkaline, decinormal solution of arsenious oxide instead of sodium thiosulphate. Compare your results in the two experiments.

8. Given a solution of manganous chloride in strong HCl, potassium iodide solution, and decinormal sodium thiosulphate solution, determine the percentage purity of (a) nitre, (b) commercial sodium nitrite.

9. You are provided with solid KI, dilute sulphuric acid, and decinormal sodium thiosulphate. Determine the strength of ordinary '20 volume' hydrogen peroxide in grams per litre. Compare your result with that obtained using standard potassium permanganate.

10. You are provided with a solution A, containing the sulphate of vanadium in the divalent state, which may be oxidized to the quinquevalent state by $KMnO_4$. You are also supplied with accurately

decinormal solutions of potassium permanganate, and sodium thiosulphate ; and an approximately decinormal solution of ferric sulphate (in 2N, sulphuric acid), and an approximately decinormal solution of iodine in KI solution.

You are required to investigate the oxidation of A produced by titrating aliquot portions of it with the ferrous sulphate and iodine respectively.

11. Given decinormal solutions of iodine and sodium thiosulphate determine the percentage of tin in stannous chloride.

12. By means of KI and decinormal sodium thiosulphate determine the percentage of iron in iron alum. Compare your result with that obtained by the potassium permanganate method.

13. You are provided with solid KI and decinormal sodium thiosulphate, and are required to determine the amount of cupric hydroxide precipitated with the amount of decinormal ammonium hydroxide added to an approximately decinormal solution of $CuSO_4.5H_2O$. Plot your results in the form of a curve.

Take 25 c.c. of the copper sulphate solution, add excess KI, and titrate with decinormal thiosulphate. To further portions of 25 c.c. of the solution, add excess KI, and 5, 10, 15, 20, and 25 c.c. respectively of decinormal ammonium hydroxide, and titrate with the decinormal thiosulphate.

14. You are provided with decinormal solutions of iodine and alkaline arsenite. Determine the strength of the bench NaOH.

15. Prepare $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ normal solutions of aluminium sulphate. Prepare also a potassium iodide-iodate mixture (as directed in § 84), and, by means of this solution, determine the degree of hydrolysis of the aluminium sulphate at each concentration, by titrating the liberated iodine with the decinormal sodium thiosulphate solution. Plot your results in the form of a curve.

16. Repeat experiment 15 with solutions of (a) cobalt sulphate, (b) nickel sulphate, and (c) ferrous sulphate. Use the same range of concentrations as in experiment 15.

17. You are provided with solid KI, dilute sulphuric acid, and decinormal sodium thiosulphate. Determine the strengths, in grams per litre, of (a) a solution of potassium permanganate, and (b) a solution of potassium dichromate.

N.B.—Potassium permanganate and dichromate react with KI in the presence of sulphuric acid, according to the equations :

(a) $2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$
(b) $K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$
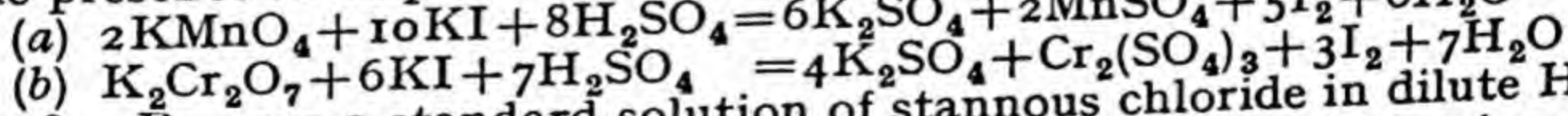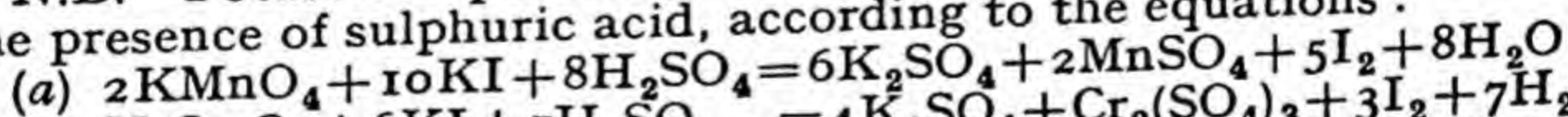
18. Prepare a standard solution of stannous chloride in dilute HCl. Use this solution, with decinormal iodine solution, to determine the amount of $KClO_3$ in 100 grams of commercial potassium chlorate.

CHAPTER VI

VOLUMETRIC DETERMINATIONS INVOLVING THE USE OF STANDARD SOLUTIONS OF SILVER NITRATE, SODIUM CHLORIDE, AND AMMONIUM THIOCYANATE; BASED UPON PRECIPITATION METHODS

86. THE USES OF STANDARD SILVER NITRATE SOLUTION. Standard silver nitrate solution is employed in the determination of soluble inorganic halides, alkali cyanides, and various indirect determinations based on these methods. For example, in the estimation of a solution of sodium chloride, the standard silver nitrate solution is run into a *neutral solution* of the chloride until the precipitation of the chlorine as silver chloride is complete. The reaction may be represented in the following manner:

$$\overset{+}{Ag} + \overset{-}{NO_3} + \overset{+}{Na} + \overset{-}{Cl} = AgCl + \overset{+}{Na} + \overset{-}{NO_3}.$$
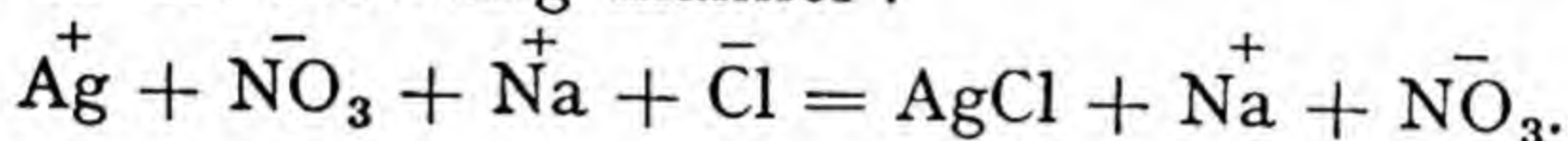
The exact 'end-point' is, however, rather difficult to determine unless another substance is employed as an indicator. The indicator in common use is potassium chromate, K_2CrO_4, in *neutral solution*. A drop of the chromate solution is added to the chloride solution until the liquid is just tinged a faint yellow, and the solution is then titrated with the standard silver nitrate solution; as long as there are free chlorine ions in the solution the silver ions from the silver nitrate will combine with them to form silver chloride in preference to combining with the $\overset{=}{CrO_4}$ ions, but, as soon as all the chlorine ions have been removed, the addition of one more drop of silver nitrate will cause a red precipitate of silver chromate. The 'end-point' of the titration is, thus, indicated by the appearance of a faint, permanent, reddish tinge.

The principle of *Fractional Precipitation* upon which the above method depends is governed by the product of the concentrations of the respective ions in the reacting solutions. For example, in the case of sodium chloride in aqueous solution, the salt is dissociated into electropositive sodium ions and electronegative chlorine ions, viz.:
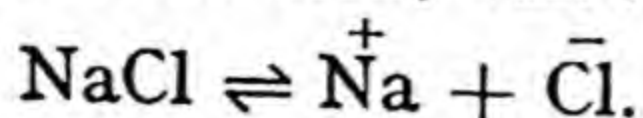
$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl}.$$

Let [NaCl] denote the concentration of the sodium chloride,

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$[\overset{+}{Na}]$ the concentration of the sodium ions, and $[\overset{-}{Cl}]$ the concentration of the chlorine ions. Then, according to Ostwald's dilution law,

$$\frac{[\overset{+}{Na}][\overset{-}{Cl}]}{[NaCl]} = K.$$

Now, in a saturated solution, the concentration [NaCl] is fixed, K is constant ; therefore, the ionic product $[\overset{+}{Na}][\overset{-}{Cl}]$ is also constant. This ionic product is known as the *real solubility* or the *solubility product*, and it is therefore constant for a saturated solution of an electrolyte ; moreover, when the value of this solubility product is exceeded precipitation will take place.

By the application of this principle we can explain the phenomenon of fractional precipitation which enables potassium chromate to be used as an indicator in the titration of soluble inorganic halides by silver nitrate.

Although we commonly regard silver chloride as an insoluble salt, it is, in reality, soluble in water to a very slight, but, nevertheless, very important, extent.

Actually, the solubility of AgCl is 0·00001 gram-molecule at 18° C.

Thus, in a saturated solution of AgCl (which we are always dealing with when titrating a chloride solution with AgNO₃) we have :

$$AgCl \leftrightharpoons \overset{+}{Ag} + \overset{-}{Cl},$$
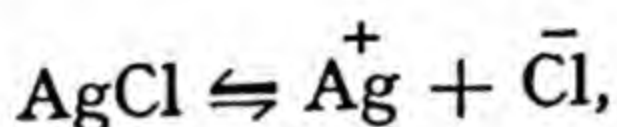
and the solubility product $[\overset{+}{Ag}][\overset{-}{Cl}]$ is constant.

Now, since the solubility of AgCl is 0·00001 gram-molecule at 18° C., the concentration (in gram-molecules) of the $\overset{+}{Ag}$ ion will be 0·00001, and, similarly, the concentration of the $\overset{-}{Cl}$ ion will also be 0·00001.

Thus, the solubility product of AgCl is [0·00001][0·00001] or 10^{-10}.

Similarly, silver chromate is soluble to the extent of 0·00008 gram-molecule at 18° C. Thus, in a saturated solution of the salt, we have

$$Ag_2CrO_4 \leftrightharpoons \overset{+}{Ag} + \overset{+}{Ag} + \overset{=}{CrO_4},$$
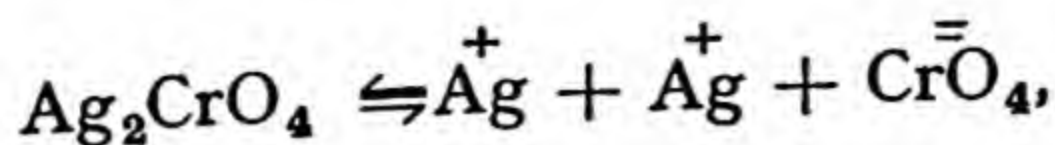
and the solubility product $[\overset{+}{Ag}]^2[\overset{=}{CrO_4}]$ is constant.

Then, since the solubility of silver chromate, at 18° C., is

0·00008 gram-molecule, the molecular concentration of the $\overset{+}{Ag}$ ions will be 2 × 0·00008, or 0·00016 ; and the molecular concentration of the $\overset{=}{CrO_4}$ ions will be 0·00008.

Thus, the solubility product is $[0·00016]^2[0·00008]$, or $2 × 10^{-12}$.

In the titration of a soluble chloride by silver nitrate, using K_2CrO_4 as the indicator, the $\overset{+}{Ag}$ ion is in equilibrium with both the AgCl and the Ag_2CrO_4 in solution, and, consequently, we can calculate the ratio of the $\overset{+}{Ag}$ ion in equilibrium with the AgCl to the $\overset{+}{Ag}$ ion in equilibrium with the Ag_2CrO_4 (remembering that 2 molecules of AgCl are equivalent to 1 molecule of Ag_2CrO_4).

This ratio will be
$$= \frac{[\overset{+}{Ag}][\overset{-}{Cl}][\overset{+}{Ag}][\overset{-}{Cl}]}{[Ag^+]^2[CrO_4^=]},$$
$$= \frac{[10^{-10}]^2}{2 × 10^{-12}},$$
$$= \frac{1}{2 × 10^8}.$$

Thus, in the supernatant liquid, the ratio of the $\overset{+}{Ag}$ ion combined with the $\overset{-}{Cl}$ ion to the $\overset{+}{Ag}$ ion combined with the $\overset{=}{CrO_4}$ ion is $1 : 2 × 10^8$, and, when this ratio is reached in the titration, the silver chromate is precipitated.

In the same way a value can be obtained for the titration of a bromide or an iodide by means of silver nitrate, employing potassium chromate as an indicator.

PRECAUTIONS TO BE OBSERVED WHEN TITRATING WITH SILVER NITRATE

(1) The titration must always be carried out in *neutral solution*, and the potassium chromate solution used as the indicator must also be neutral, as silver chromate is soluble in acids. Consequently, if the solution is acid it must be carefully neutralized by the addition of sodium carbonate solution.

(2) The titration must be carried out in the *cold*, as the solubility of the silver chromate is affected by a rise of temperature.

(3) Only a small amount of potassium chromate solution must be added to the reacting solutions : just sufficient to tinge the liquid a faint yellow.

(4) As the 'end-point' of the reaction (in titrating a halide) is indicated when a slight *excess* of silver nitrate has been added, the titration must be carried out very carefully to minimize error.

PREPARATION OF DECINORMAL SILVER NITRATE SOLUTION

In the reaction :

$$\overset{+}{Na} + \overset{-}{Cl} + \overset{+}{Ag} + \overset{-}{NO_3} = AgCl + \overset{+}{Na} + \overset{-}{NO_3}$$
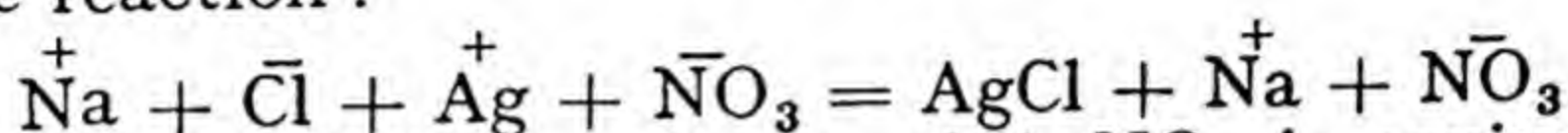
it will be seen that 1 molecule of $AgNO_3$ is equivalent to 1 atom of chlorine. Consequently, a normal solution of $AgNO_3$ will be a molar solution, and, therefore, a decinormal solution of the salt will contain one-tenth of the formula weight of $AgNO_3$ per litre, i.e. 17 grams.

Just over 8·5 grams of the pure, recrystallized $AgNO_3$ are weighed accurately, dissolved in cold distilled water, and diluted to the required volume. For example, suppose that 8·535 grams of the crystals were taken, dissolved in distilled water, and diluted to 500 c.c.

Then, the normality of the solution is

$$0·1N. \times \frac{8·535}{8·5}.$$

Thus, 8·535 grams of $AgNO_3$ would be contained in $500 \times \frac{8·535}{8·5}$, or 502 c.c., of decinormal $AgNO_3$ solution. 500 c.c. of the silver nitrate solution would then be diluted to 502 c.c. and labelled 0·1N.$AgNO_3$.

87. The Determination of Soluble Halides. Any soluble inorganic halide may be estimated directly by titration with decinormal silver nitrate solution, using potassium chromate as the indicator in neutral solution.

For example, in the case of sodium chloride, the reaction may be written :

$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl}$$
$$AgNO_3 \rightleftharpoons \overset{-}{NO_3} + \overset{+}{Ag}$$
$$\Downarrow$$
$$AgCl$$
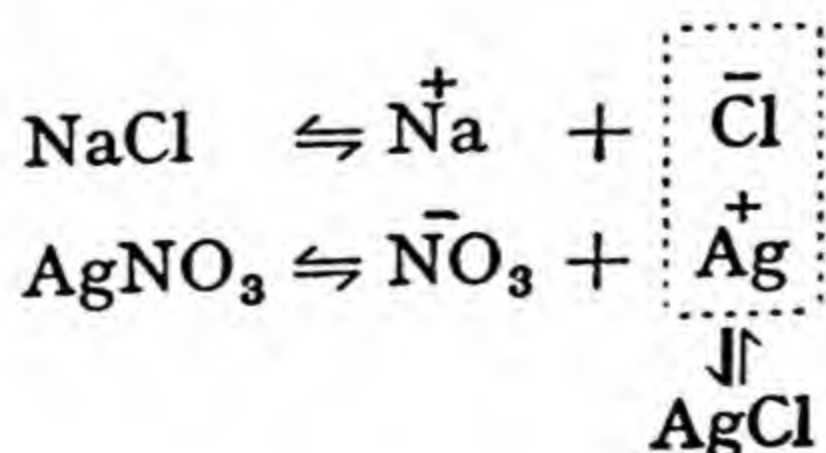
To Estimate a Solution of Potassium Bromide. A portion of the bromide solution is, first of all, tested for free acid, and, if the test is positive, the solution is carefully neutralized by means of dilute sodium carbonate solution, employing methyl orange as the indicator. Aliquot portions of the neutral bromide solution are then titrated with $0.1N.AgNO_3$ solution, using 1 or 2 drops of neutral K_2CrO_4 solution as the indicator ; the ' end-point ' of the reaction being indicated when a faint, permanent reddish tinge of silver chromate is produced in the liquid.

Suppose, for example, that 25 c.c. of the solution of potassium bromide required a mean volume of 18·7 c.c. of $0.1N.AgNO_3$ to precipitate all the KBr as AgBr.

Then 1 litre of the solution would need 40 × 18·7, or 748 c.c., of $0.1N.AgNO_3$.

Now, $$AgNO_3 \equiv Br \equiv KBr.$$

Thus, 170 grams of $AgNO_3$ are equivalent to 119 grams of KBr. Therefore, 1 litre of $0.1N.AgNO_3$ is equivalent to 11·9 grams of KBr.

Therefore, 748 c.c. of $0.1N.AgNO_3$ are equivalent to 11·9 × 0·748, or 8·90 grams, of KBr.

Thus, the given solution contains *8·90 grams of KBr per litre.*

88. TO DETERMINE THE PERCENTAGE OF CHLORINE IN SODIUM CHLORIDE. About 1 gram of the pure sodium chloride is weighed accurately, dissolved in distilled water, and diluted to 250 c.c. If necessary, the solution is neutralized before diluting to the above volume. Aliquot portions of 50 c.c. of the chloride solution are then titrated with $0.1N.AgNO_3$ using 1 or 2 drops of neutral K_2CrO_4 solution as the indicator. At least three concordant results are obtained, and the amount of chlorine is determined from the titration values employing the equivalents :

$$AgNO_3 \equiv Cl ;$$
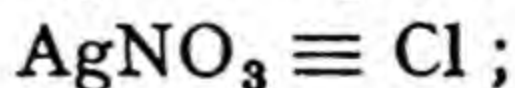
i.e. 1 litre of $0.1N.AgNO_3$ is equivalent to 3·55 grams of Cl.

For example, in an experiment, 1·180 grams of sodium chloride were dissolved in distilled water, neutralized with dilute Na_2CO_3 solution, and diluted to 250 c.c. As a mean of three titrations, 50 c.c. of the solution required 26·2 c.c. of $0.1N.AgNO_3$ to effect the reddish tinge with K_2CrO_4.

Thus, 250 c.c. of the solution would require 5 × 26·2, or 131 c.c., of $0.1N.AgNO_3$. And, since 1 litre of $0.1N.AgNO_3$

is equivalent to 3·55 grams of Cl, 131 c.c. of 0·1N.AgNO$_3$ would be equivalent to 3·55 × 0·131, or 0·465 gram, of Cl.

Therefore, the percentage of chlorine in NaCl is

$$\frac{0·465}{1·180} \times 100, \text{ or } 39·3\%.$$

89. THE ESTIMATION OF CHLORINE IN A NATURAL WATER. For this purpose a centinormal solution of AgNO$_3$ is generally to be preferred : this is easily prepared by taking a suitable volume of decinormal AgNO$_3$ and diluting it tenfold with distilled water. Moreover, as it is customary to express the result in grains per gallon, it is convenient to titrate 70 c.c. of the solution at a time ; one gallon of water weighs 70,000 grains, and as 70 c.c. of water weigh 70,000 milligrams the answer can then be expressed directly in parts of chlorine per 70,000 parts of water, i.e. in grains per gallon.

As in the previous determinations, the solution must be tested for neutrality, and if it is acid (as is frequently the case) it must be carefully neutralized by the addition of dilute Na$_2$CO$_3$ solution, using methyl orange as the indicator.

For example, it was found that, as a mean of three titrations, 70 c.c. of a specimen of a mineral water required 67·6 c.c. of 0·01N.AgNO$_3$ to effect the permanent reddish tinge, with neutral K$_2$CrO$_4$ as the indicator.

Now, 1 litre of 0·01N.AgNO$_3$ is equivalent to 0·355 gram of Cl. Therefore 67·6 c.c. of 0·01N.AgNO$_3$ are equivalent to 0·355 × 0·0676 × 1000, or 24 milligrams, of Cl.

Thus the mineral water contains *24 grains of chlorine per gallon*.

90. THE DETERMINATION OF A MIXTURE OF TWO HALIDES. As in the determination of a mixture of acids by means of standard alkali (§ 24 ; see also §§ 25 and 26), the total weight of the halides must be known, and the accuracy of the method depends upon the difference between the equivalents of the respective halides ; the greater this difference the more accurate is the result. Accuracy in titration is also very important, since a small error will introduce a comparatively large error in the calculation. It must therefore be borne in mind that this method of determination is only an approximate one.

A known weight of the mixture is dissolved in distilled water, neutralized, if necessary, as described in the preceding determinations, and diluted to a convenient volume. Aliquot

portions of the solution are then titrated with $0 \cdot 1N.AgNO_3$, using neutral K_2CrO_4 as the indicator ; e.g. :

To Estimate a Mixture of Sodium Chloride and Potassium Iodide. The proportions of NaCl and KI respectively in a solution of the mixture are calculated as follows :

Let x be the amount of NaCl in 1 litre of the solution, and

Let y be the amount of KI in 1 litre of the solution.

Then the amounts of each halide in 1 litre of the solution can be calculated from the following simultaneous equations :

$$x + y = m_1 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(a)$$

$$\frac{170x}{58 \cdot 5} + \frac{170y}{166} = m_2 \dots\dots\dots\dots\dots\dots\dots\dots(b)$$

where m_1 denotes the weight of mixed halides in 1 litre of the solution, and m_2 the weight of $AgNO_3$ required to completely precipitate all the halogen in 1 litre of the solution as silver halide. In (b), 170, 58·5, and 166 are the chemical equivalents of $AgNO_3$, NaCl, and KI respectively.

Method. An accurately known weight of the mixture is dissolved in distilled water, neutralized, if necessary, by the addition of dilute Na_2CO_3 solution as described in the previous determinations, and diluted to a convenient volume. Aliquot portions of this solution are then titrated with $0 \cdot 1N.AgNO_3$, using one or two drops of neutral K_2CrO_4 as the indicator. The amounts of each halide are then determined from the titration values, employing the above simultaneous equation.

For example, 5·84 grams of the mixture of NaCl and KI were dissolved in distilled water, neutralized as described above, and diluted to 250 c.c. Therefore $m_1 = 5\cdot84 \times 4$, or 23·36 grams.

As a mean of three titrations, 25 c.c. of this solution required 51·0 c.c. of $0\cdot1N.AgNO_3$ to effect the reddish tinge with the K_2CrO_4.

Thus, 1 litre of the solution would require 40×51, or 2040 c.c., of $0\cdot1N.AgNO_3$.

Now 1 litre of $0\cdot1N.AgNO_3$ contains 17 grams of $AgNO_3$. Therefore 2·04 litres of $0\cdot1N.AgNO_3$ contain $17 \times 2\cdot04$, or 34·68 grams, of $AgNO_3$.

Consequently, $m_2 = 34\cdot68$ grams.

Substituting these values in the above simultaneous equation, we get

$$x + y = 23\cdot36.$$

$$\frac{170x}{58\cdot5} + \frac{170y}{166} = 34\cdot68.$$

From which $x = 5.70$ and $y = 17.66$ grams respectively.

Therefore, the percentage of NaCl in the mixture is $\dfrac{570}{23.36}$, or 24.4%, and the percentage of KI in the mixture is $\dfrac{1766}{23.36}$, or 75.6%.

91. THE DETERMINATION OF ALKALI CYANIDES. If *excess of silver nitrate* solution is added to a solution of an alkali cyanide, a precipitate of silver cyanide is formed according to the equation (in the case of sodium cyanide) :

$$NaCN \rightleftharpoons \overset{+}{Na} + \overline{CN}$$

$$AgNO_3 \rightleftharpoons \overline{NO_3} + \overset{+}{Ag}$$

$$\Downarrow$$

$$AgCN \dots\dots\dots\dots(1)$$
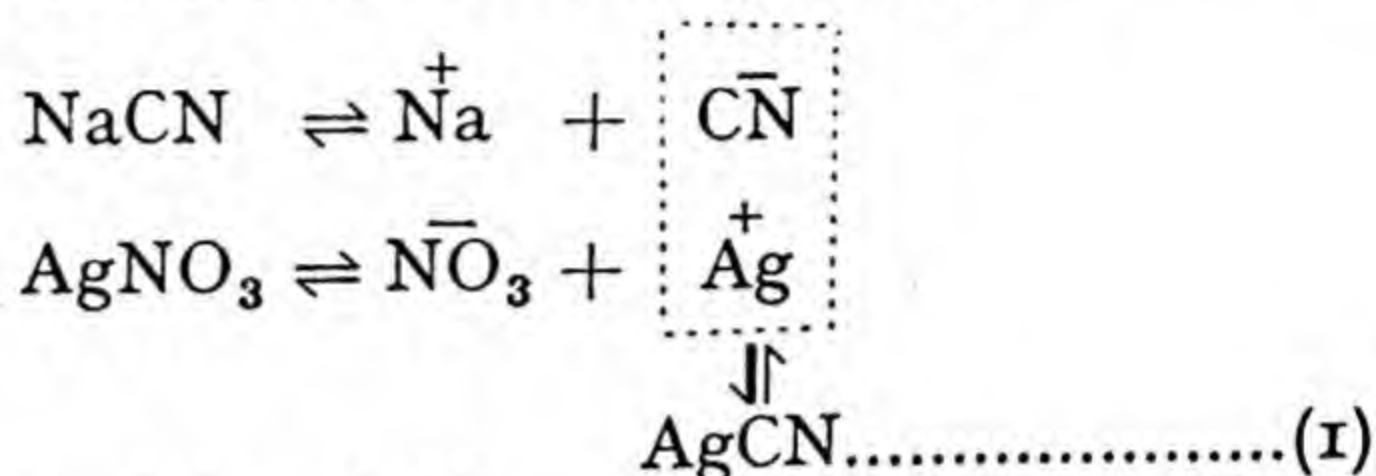
If, however, *excess of the alkali cyanide* be present, the silver cyanide dissolves in the excess of sodium cyanide forming the double cyanide $NaAg(CN)_2$. Thus, in this case, the equation must be represented by the equation :

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3 \dots\dots(2)$$
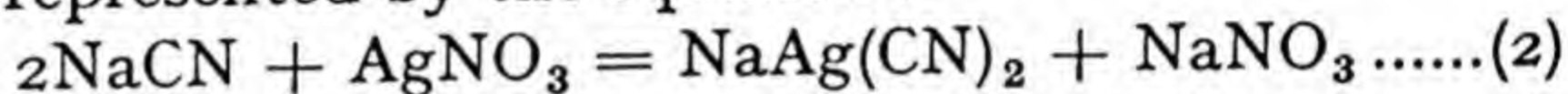
It will be observed that the double cyanide is composed of 1 molecule of NaCN associated with 1 molecule of AgCN. When, however, 1 molecule of the excess NaCN has ' dissolved ' 1 molecule of AgCN, the slightest addition of silver nitrate solution will result in the decomposition of the double cyanide with the precipitation of AgCN according to the equation :

$$NaAg(CN)_2 + AgNO_3 = 2AgCN + NaNO_3 \dots\dots(3)$$
$$\downarrow$$
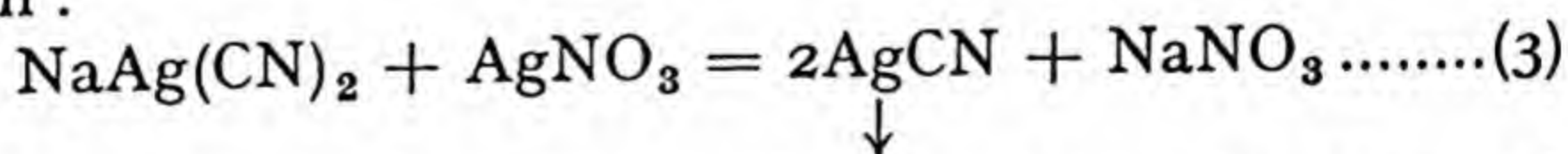
Consequently, in titrating a solution of an alkali cyanide with standard silver nitrate solution, the ' end-point ' of reaction (2) may be indicated by the beginning of reaction (3) ; i.e. when the addition of 1 drop of the silver nitrate solution produces a permanent precipitate of silver cyanide. An obvious precipitate means that the ' end-point ' has been overreached, and a *slight turbidity* of the solution *only* should be obtained in an accurate determination. The cyanide is then estimated from the titration values, employing (in the case of NaCN) the equivalents :

$$AgNO_3 \equiv 2NaCN \text{ from equation (2) ; e.g.}$$
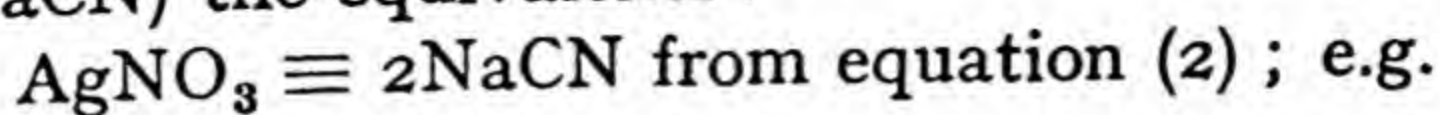
To Determine the Percentage of Cyanogen in Pure KCN.
An accurately known weight of the pure cyanide is dissolved
in distilled water and diluted to a convenient volume. Aliquot
portions of the solution are then titrated with $0.1N.AgNO_3$
solution and the ' end-point ' is marked by the production of
a faint, permanent turbidity of the solution, due to the com-
mencement of the precipitation of the AgCN. The amount
of cyanogen is then determined from the mean titration value,
employing the equivalents :

$$AgNO_3 \equiv 2KCN \equiv (CN)_2 ;$$

i.e. 170 grams of $AgNO_3$ are equivalent to 52 grams of $(CN)_2$;
or 1 litre of $0.1N.AgNO_3$ is equivalent to 5.2 grams of $(CN)_2$.

For example, 1.097 grams of pure KCN were dissolved in
distilled water and diluted to 250 c.c. As a mean of three
titrations, 50 c.c. of the cyanide solution required 22.4 c.c. of
$0.1N.AgNO_3$ to produce a faint, permanent turbidity in the
solution.

Thus, 250 c.c. of the solution would need 22.4×5, or
112 c.c., of $0.1N.AgNO_3$.

Then, since 1 litre of $0.1N.AgNO_3$ is equivalent to 5.2 grams
of $(CN)_2$, 112 c.c. of $0.1N.AgNO_3$ are equivalent to 5.2×0.112,
or 0.582 gram, of $(CN)_2$.

Therefore, the percentage of cyanogen in pure potassium
cyanide is
$$\frac{0.582}{1.097} \times 100, \text{ or } 53.1\%.$$

(For another method of estimating alkali cyanides see
§ 100.)

92. THE DETERMINATION OF CHLORATES. When potas-
sium chlorate is heated it decomposes, the final products
being potassium chloride and oxygen, viz. :

(a) $4KClO_3 = 3KClO_4 + KCl.$
(b) $KClO_4 = KCl + 2O_2.$

The complete reaction may therefore be written :

$$2KClO_3 = 2KCl + 3O_2.$$
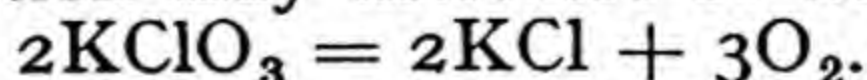
If, therefore, a chlorate is heated until it is completely
decomposed, and the residual chloride dissolved in distilled
water, it can be estimated as a chloride by means of standard
$AgNO_3$; e.g.

To Determine the Purity of a Sample of Potassium Chlorate.
A portion of the chlorate is weighed accurately in a tared
crucible, and is then ignited carefully to constant weight.
The residue, when cool, is extracted with distilled water,

neutralized, if necessary, as described in § 87, and diluted to a suitable volume. Aliquot portions of this solution are then titrated with decinormal silver nitrate solution, using 1 or 2 drops of dilute neutral K_2CrO_4 solution as the indicator, in the usual manner. The amount of chlorate is then determined from the mean titration value employing the equivalents :

$$AgNO_3 \equiv Cl \equiv KClO_3.$$
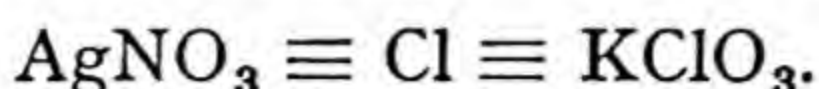
Thus, 170 grams of $AgNO_3$ are equivalent to 122·5 grams of $KClO_3$; i.e. 1 litre of 0·1N.$AgNO_3$ is equivalent to 12·25 grams of $KClO_3$.

For example, 3·315 grams of pure $KClO_3$ were ignited to constant weight and the residual chloride made up to 250 c.c. as described above. As a mean of three titrations, 25 c.c. of this solution required the addition of 25·8 c.c. of 0·1N.$AgNO_3$ to effect the colour change with K_2CrO_4.

Thus, 250 c.c. of the solution would need 258 c.c. of 0·1N.$AgNO_3$.

Then, since 1 litre of 0·1N.$AgNO_3$ is equivalent to 12·25 grams of $KClO_3$, 258 c.c. of 0·1N.$AgNO_3$ are equivalent to 12·25 × 0·258, or 3·160 grams, of $KClO_3$.

Thus the percentage of $KClO_3$ in the sample of potassium chlorate is

$$\frac{3 \cdot 160}{3 \cdot 315} \times 100, \text{ or } 98 \cdot 4\%.$$

INDIRECT DETERMINATIONS BY MEANS OF STANDARD SILVER NITRATE

Any metal which forms an insoluble carbonate and a soluble chloride may readily be estimated indirectly by means of standard silver nitrate solution ; e.g. the amount of carbon dioxide in most carbonates ; the alkali salts of some organic acids (which are converted into carbonates on ignition), etc., can also be determined in this way. The method is based upon decomposition with HCl with the formation of a soluble chloride. The chloride is then estimated by means of standard silver nitrate in the usual way. A few typical indirect estimations with standard silver nitrate are given below.

93. THE ESTIMATION OF BARIUM IN BARIUM CARBONATE. An accurately known weight of the pure carbonate is dissolved in HCl and evaporated to dryness, care being taken to avoid

loss by spitting (the evaporation should be performed on the water bath) :

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$
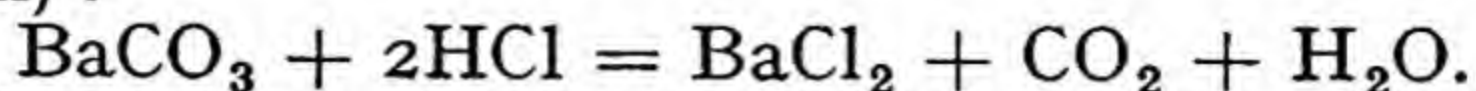
The residual barium chloride is dissolved in distilled water and again evaporated to dryness on the water bath ; this step is necessary in order to expel the traces of acid which are to be found in the first residue of the barium chloride. The $BaCl_2$ is then dissolved in distilled water, and tested for neutrality ; if the solution is still acid it is neutralized by the addition of dilute sodium carbonate solution using methyl orange as an indicator. The neutral solution is then diluted to a convenient volume, and aliquot portions are titrated with $0.1N.AgNO_3$, using 1 or 2 drops of neutral K_2CrO_4 as the indicator. The barium is then estimated from the mean titration value employing the equivalents :

$$2AgNO_3 \equiv Ba.$$
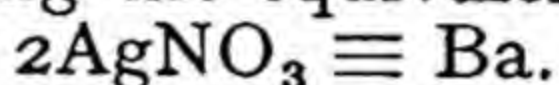
Thus, 2 × 170 grams of $AgNO_3$ are equivalent to 137·4 grams of Ba ; i.e. 1 litre of $0.1N.AgNO_3$ is equivalent to 6·87 grams of Ba.

For example, in an experiment, 3·908 grams of pure, precipitated barium carbonate were converted into a neutral solution of barium chloride as described above. The volume of the solution was 500 c.c. It was found, as a mean of three titrations, that 25 c.c. of the chloride solution required 19·8 c.c. of $0.1N.AgNO_3$ to effect the reddish tinge with K_2CrO_4. Therefore, 500 c.c. of the chloride solution would need 20 × 19·8, or 396 c.c. of $0.1N.AgNO_3$.

Then, since 1 litre of $0.1N.AgNO_3$ is equivalent to 6·87 grams of Ba, 396 c.c. of $0.1N.AgNO_3$ are equivalent to 6·87 × 0·396, or 2·720 grams, of Ba.

Therefore the percentage of barium in barium carbonate is

$$\frac{2.720}{3.908} \times 100, \text{ or } 69.6\%.$$

94. THE DETERMINATION OF CARBON DIOXIDE IN A SOLUBLE CARBONATE. A solution of a carbonate, of known strength, is precipitated as barium carbonate by the addition of excess of barium chloride solution ; e.g.

$$K_2CO_3 \rightleftharpoons \overset{+}{K} + \overset{+}{K} + \overset{=}{CO_3}$$

$$BaCl_2 \rightleftharpoons \overset{-}{Cl} + \overset{-}{Cl} + \overset{++}{Ba}$$

$$\downarrow$$

$$BaCO_3$$
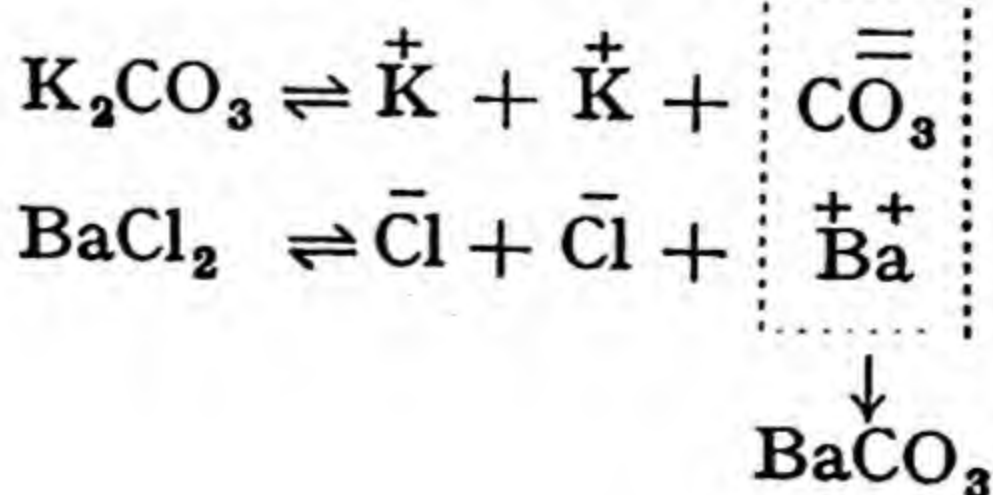
The precipitated barium carbonate is filtered, washed, and dissolved in HCl, viz. :

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$
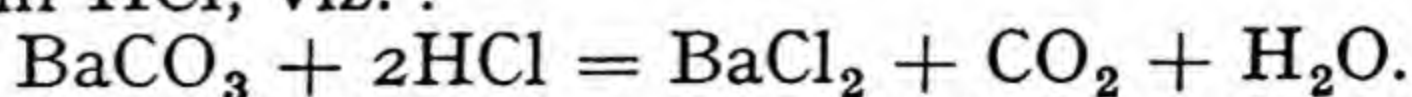
The resulting solution is evaporated to dryness on the water bath, and the residual chloride is dissolved in distilled water and again evaporated to dryness in order to eliminate traces of HCl. The final residue is then dissolved in distilled water, and the last trace of acid destroyed, if necessary, by the addition of dilute sodium carbonate solution, using methyl orange as the indicator. The solution is then diluted to a suitable volume, and aliquot portions are titrated with $0.1N.AgNO_3$, using one or two drops of dilute, neutral K_2CrO_4 solution as the indicator. The amount of carbon dioxide is then determined from the mean titration value, employing the equivalents :

$$2AgNO_3 \equiv 2HCl \equiv CO_2.$$

Thus, 170 grams of $AgNO_3$ are equivalent to 22 grams of CO_2 ; i.e. 1 litre of $0.1N.AgNO_3$ is equivalent to 2.2 grams of CO_2.

For example, 1.172 grams of anhydrous potassium carbonate were dissolved in water, precipitated as barium carbonate, and converted to 250 c.c. of barium chloride solution as described above. As a mean of three titrations, it was found that 25 c.c. of the chloride solution required 17.0 c.c. of $0.1N.AgNO_3$ to effect the reddish tinge with K_2CrO_4.

Thus, 250 c.c. of the chloride solution would need 170 c.c. of $0.1N.AgNO_3$.

Then, since 1 litre of $0.1N.AgNO_3$ solution is equivalent to 2.2 grams of CO_2, 170 c.c. of $0.1N.AgNO_3$ will be equivalent to 2.2×0.170, or 0.374 grams of CO_2.

Therefore, the percentage of carbon dioxide in anhydrous K_2CO_3 is

$$\frac{0.374}{1.172} \times 100, \text{ or } 31.9\%.$$

95. THE INDIRECT DETERMINATION OF THE ALKALI SALTS OF SOME ORGANIC ACIDS. The method is based upon the fact that the alkali salts of many organic acids yield carbonates on ignition. The estimation then proceeds as in the case of a carbonate (§ 93 or § 94).

For example, calcium acetate, on dry distillation, yields calcium carbonate with the evolution of acetone, viz. :

$$\begin{array}{c}CH_3COO \\ \diagdown \\ CH_3COO \diagup\end{array} Ca = \begin{array}{c}CH_3 \\ \diagdown \\ CH_3 \diagup\end{array} CO + CaCO_3.$$
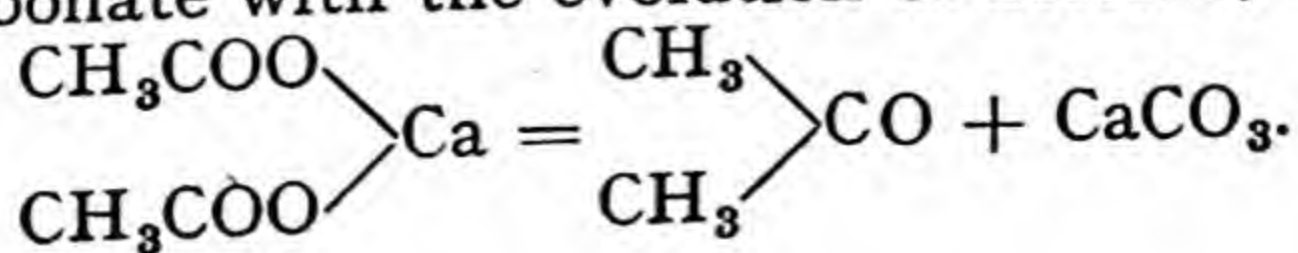
In a similar manner the oxalate of an alkali metal yields a carbonate and carbon monoxide, when ignited, viz. :

$$\begin{array}{l} \text{COONa} \\ | \qquad = Na_2CO_3 + CO. \\ \text{COONa} \end{array}$$
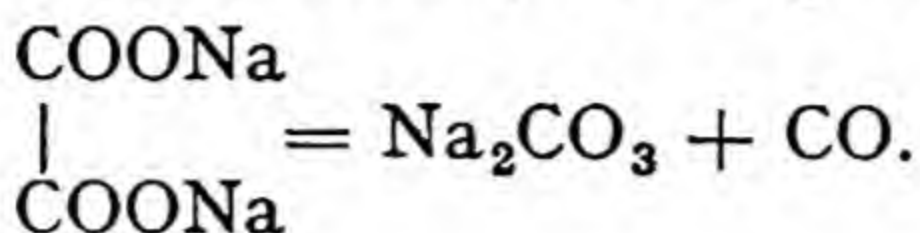
VOLUMETRIC ESTIMATIONS WITH STANDARD SODIUM CHLORIDE SOLUTION

96. THE USES OF STANDARD NaCl SOLUTION. By a reversal of the method of estimating a solution of sodium chloride by means of standard silver nitrate solution, silver, in its soluble salts, may be determined by titration with a standard solution of sodium chloride.

Preparation of the 0·1N.NaCl Solution. The equivalent weight of NaCl is 58·5, and a decinormal solution will contain, therefore, 5·85 grams of NaCl per litre. It is best to weigh accurately about 6 grams of the pure sodium chloride, dilute to 1 litre with distilled water, and standardize the solution by means of 0·1N.AgNO$_3$ solution, using 1 or 2 drops of the neutral K$_2$CrO$_4$ solution as the indicator. The solution is then diluted by the addition of the calculated amount of distilled water.

Method of Using Decinormal NaCl Solution. In estimating the amount of silver in a given solution, neutral K$_2$CrO$_4$ is used as the indicator as in the determination of halides by means of standard silver nitrate solution. To ensure accuracy, however, the unknown silver solution must be run into a measured volume of the 0·1N.NaCl solution, to which 1 or 2 drops of the indicator have been added, until the faint, permanent reddish tinge appears. If the indicator is added to the silver solution and the standard NaCl solution then run in, the 'end-point' is unsatisfactory. Here, again, both the reacting solutions must be neutral.

To Determine the Percentage of Silver in Silver Nitrate. An accurately known weight of the pure, recrystallized silver nitrate is dissolved in distilled water, neutralized, if necessary, by the addition of dilute sodium carbonate solution, using methyl orange as the indicator, and diluted to a convenient volume. 25 c.c. of the 0·1N.NaCL solution are transferred to a small flask, a few drops of neutral K$_2$CrO$_4$ solution added as the indicator, and the silver nitrate solution run in from a burette until the reddish tinge is obtained. Three concordant

9

results are obtained, and the silver estimated from the mean titration value employing the equivalents :
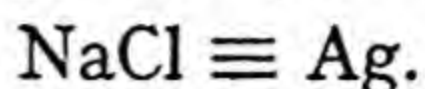
$$NaCl \equiv Ag.$$

Thus, 58·5 grams of NaCl are equivalent to 108 grams of Ag ; i.e. 1 litre of 0·1N.NaCl is equivalent to 10·8 grams of Ag.

For example, 5·316 grams of pure $AgNO_3$ were dissolved in distilled water, neutralized as described above, and diluted to 250 c.c.   It was found that, as a mean of three determinations, 25 c.c. of 0·1N.NaCl needed the addition of 20·0 c.c. of the silver solution to produce the reddish tinge with K_2CrO_4.

Thus, 250 c.c. of the silver solution would require $\frac{25}{20} \times 250$, or 312·5 c.c., of 0·1N.NaCl.

Then, since 1 litre of 0·1N.NaCl is equivalent to 10·8 grams of Ag, 312·5 c.c. of 0·1N.NaCl are equivalent to 10·8 × 0·3125, or 3·375 grams, of Ag.

Therefore, the percentage of silver in silver nitrate is

$$\frac{3·375}{5·316} \times 100, \text{ or } 63·5\%.$$

VOLUMETRIC DETERMINATIONS WITH STANDARD AMMONIUM THIOCYANATE

97. THE USES OF STANDARD AMMONIUM THIOCYANATE SOLUTION. Any volumetric determination which can be carried out with standard silver nitrate or sodium chloride solutions may also be performed, either directly or indirectly, by means of a standard solution of ammonium thiocyanate. The solution is used in two main ways : (a) *In the determination of silver in its alloys or soluble salts, or* (b) *in the indirect determination of halides.* The method is based upon the reaction of silver nitrate with ammonium thiocyanate to give a sparingly soluble precipitate of silver thiocyanate according to the equation :

$$AgNO_3 \ \rightleftharpoons \ \overset{+}{Ag} + \overset{-}{NO_3}$$

$$NH_4CNS \rightleftharpoons \overset{-}{CNS} + \overset{+}{NH_4}$$

$$\Updownarrow$$
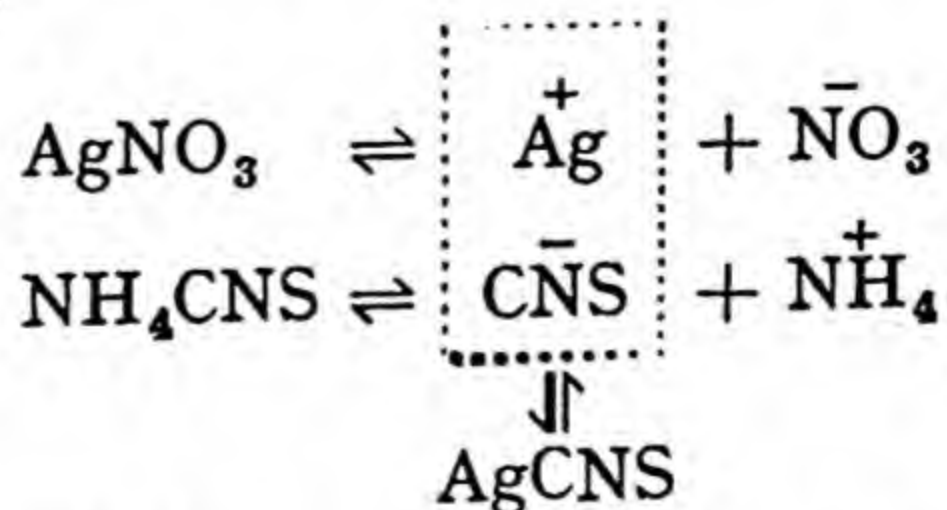
$$AgCNS$$

The 'end-point' of the reaction is indicated by adding a

little ferric sulphate to the silver nitrate solution; when all the silver has been converted to AgCNS a permanent blood-red tinge, due to the formation of ferric thiocyanate, is imparted to the liquid.

The ammonium thiocyanate method has the great advantage over the sodium chloride method for the determination of silver that the 'end-point' is unaffected by free acid at ordinary temperatures, and it is, therefore, widely used in silver determinations.

Preparation of Decinormal Ammonium Thiocyanate. Since 1 molecule of NH_4CNS is equivalent to 1 molecule of $AgNO_3$, a normal solution of ammonium thiocyanate solution will be a molar solution. A $0 \cdot 1N.NH_4CNS$ solution will contain, therefore, $7 \cdot 6$ grams of NH_4CNS per litre. The salt is, however, too deliquescent to permit accurate weighing, so about 8 grams of the salt are weighed roughly, dissolved in distilled water, and diluted to 1 litre. Aliquot portions of this solution are then titrated with $0 \cdot 1N.AgNO_3$ solution, using ferric sulphate as the indicator in the manner described above (for the preparation of the indicator see below). The NH_4CNS solution is then diluted to the calculated volume required to make it accurately decinormal.

For example, suppose that 25 c.c. of the NH_4CNS solution required a mean volume of $27 \cdot 2$ c.c. of $0 \cdot 1N.AgNO_3$ to effect the colour change with ferric sulphate.

Then $(27 \cdot 2 - 25)$, or $2 \cdot 2$ c.c., of water must be added to each 25 c.c. of the NH_4CNS solution to make it decinormal; i.e. 1 litre of the solution will require the addition of $40 \times 2 \cdot 2$, or 88 c.c., of distilled water.

The Preparation of the Indicator : Ferric Sulphate. Although any ferric salt would give a blood-red colour with NH_4CNS, ferric sulphate is used in preference to ferric chloride, since the latter would react with the silver nitrate used in the determination, giving a white precipitate of AgCl. The indicator is best prepared by dissolving one or two crystals of ferrous sulphate in an aqueous solution of nitric acid (1 volume of HNO_3 : 2 volumes of H_2O), and boiling; the ferrous sulphate is thus oxidized to ferric sulphate; the boiling is continued until all nitrous fumes have been expelled, and the solution is then diluted with its own volume of water. About 3 c.c. of this solution should be used as the indicator in each titration. It is important that, in any determination, the *same* volume of ferric sulphate solution should be used in each titration; the free nitric acid present in the indicator solution

does not affect the 'end-point' of the reaction adversely; in fact, its presence gives greater accuracy to the determination.

98. THE DETERMINATION OF SILVER IN A SILVER ALLOY. About one gram of the alloy is weighed accurately and dissolved under the action of gentle heat in dilute nitric acid. If any residue is left it is filtered, washed with distilled water, and the combined filtrate and washings diluted to a convenient volume. Aliquot portions of the diluted solution are then titrated with $0.1N.NH_4CNS$, using 3 c.c. of ferric sulphate solution as the indicator. Three concordant results are obtained (using the same amount of indicator in each titration), and the amount of silver is determined from the mean titration value employing the equivalents :

$$NH_4CNS \equiv Ag.$$

Thus, 1 litre of $0.1N.NH_4CNS$ is equivalent to 10.8 grams of Ag.

For example, in the estimation of a silver-copper alloy, 1.232 grams of the alloy were dissolved in dilute nitric acid, and, after filtration and washing of the residue, the solution was diluted to 200 c.c. As a mean of three determinations, it was found that 50 c.c. of the silver solution required 20.5 c.c. of $0.1N.NH_4CNS$ solution to effect the colour change with ferric sulphate.

Thus, 200 c.c. of the silver solution would require 4×20.5, or 82 c.c., of $0.1N.NH_4CNS$.

Then, since 1 litre of $0.1N.NH_4CNS$ is equivalent to 10.8 grams of Ag, 82 c.c. of $0.1N.NH_4CNS$ are equivalent to 10.8×0.082, or 0.886 gram, of Ag.

Thus, the percentage of silver in the alloy is

$$\frac{0.886}{1.232} \times 100, \text{ or } 71.9\%.$$

99. THE ESTIMATION OF SOLUBLE HALIDES BY MEANS OF STANDARD NH_4CNS. The method of determination consists in allowing a solution of the halide to react with a measured excess of standard $AgNO_3$ solution. The precipitated silver halide is filtered off, washed well with distilled water, and the filtrate and the washings made up to a suitable volume with distilled water. Aliquot portions of this solution are then titrated with decinormal NH_4CNS, using ferric sulphate as the indicator as described in § 97 ; the excess $AgNO_3$ is thus determined, and the halide is calculated from the titration values.

For example, in the estimation of sodium bromide, the reactions are :

(a) $\overset{+}{Na}+\overset{-}{Br}+\overset{+}{Ag}+\overset{-}{NO_3} = AgBr+\overset{+}{Na}+\overset{-}{NO_3}.$

(b) $\overset{+}{Ag}+\overset{-}{NO_3}+\overset{+}{NH_4}+\overset{-}{CNS} = AgCNS+\overset{+}{NH_4}+\overset{-}{NO_3}.$
(excess)
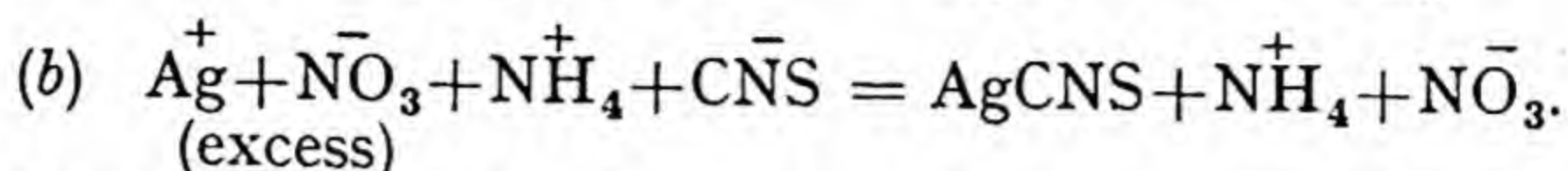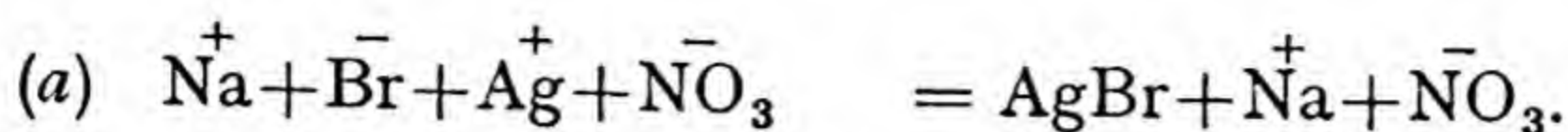
To Determine the Amount of KCl in a Cold, Saturated Solution of Potassium Chloride by Means of Decinormal NH₄CNS Solution. 25 c.c. of the saturated solution of KCl were diluted to 1 litre with distilled water. Portions of 25 c.c. of this solution were then mixed with portions of 50 c.c. of o·1N.AgNO₃ solution ; the precipitated AgCl was filtered, washed, and the combined filtrate and washings titrated with o·1N.NH₄CNS, using 3 c.c. of ferric sulphate solution as the indicator in each titration. It was found that a mean volume of 22·7 c.c. of o·1N.NH₄CNS was required to precipitate the excess AgNO₃ as AgCNS.

Therefore, 25 c.c. of the original KCl solution (1 litre of the diluted solution) would require 40 × (50 − 22·7), or 1092 c.c., of o·1N.AgNO₃ to precipitate all the KCl as AgCl.

Now, $AgNO_3 \equiv KCl.$

Thus, 170 grams of AgNO₃ are equivalent to 74·5 grams of KCl. Therefore 1 litre of o·1N.AgNO₃ is equivalent to 7·45 grams of KCl.

Thus, 1·092 litres of o·1N.AgNO₃ are equivalent to 1·092 × 7·45, or 8·135 grams, of KCl.

Therefore, 100 c.c. of a cold, saturated solution of potassium chloride contain 4 × 8·135, or *32·54 grams, of KCl.*

100. THE DETERMINATION OF ALKALI CYANIDES BY MEANS OF STANDARD NH₄CNS. In this determination the principle is similar to that in the estimation of halides by standard NH₄CNS. The aqueous solution of the cyanide is allowed to react with a known excess of standard AgNO₃ ; the cyanide is thus converted to the insoluble silver cyanide, viz. :

$$\overset{+}{K} + \overset{-}{CN} + \overset{+}{Ag} + \overset{-}{NO_3} = AgCN + \overset{+}{K} + \overset{-}{NO_3}.$$
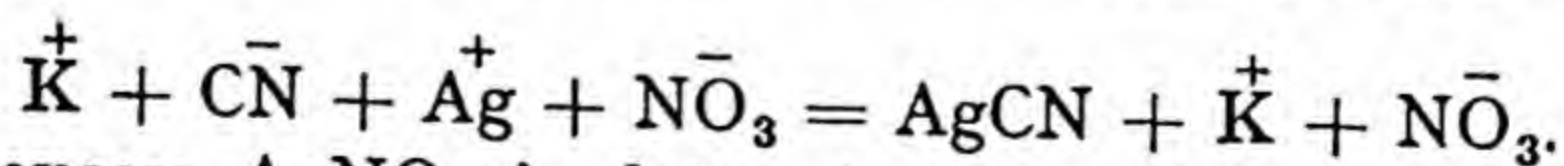
The excess AgNO₃ is determined by titration with deci-normal NH₄CNS, employing 3 c.c. of ferric sulphate solution as the indicator in each titration, viz. :

$$\overset{+}{Ag} + \overset{-}{NO_3} + \overset{+}{NH_4} + \overset{-}{CNS} = AgCNS + \overset{-}{NO_3} + \overset{+}{NH_4}.$$
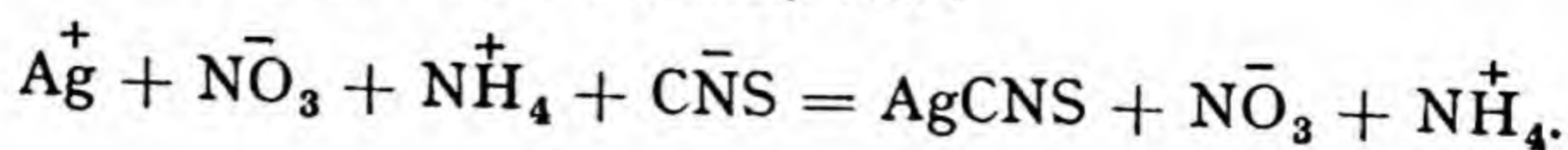
The amount of standard $AgNO_3$ equivalent to the alkali cyanide is then determined by difference ; e.g. :

To Determine the Percentage of Cyanogen in Pure KCN. The solution of KCN used in the determination of the cyanogen in KCN by the standard silver nitrate method (see § 91) was again employed. 250 c.c. of this solution contained 1·097 grams of pure KCN.

25 c.c. of the solution were mixed with 50 c.c. of 0·1N.$AgNO_3$ solution ; the insoluble silver cyanide was filtered off, washed, and the combined filtrate and washings titrated with 0·1N.NH_4CNS, using 3 c.c. of ferric sulphate solution as the indicator. As a mean of three determinations, 27·6 c.c. of 0·1N.NH_4CNS were required to effect the colour change with the ferric sulphate.

Thus, (50 − 27·6), or 22·4 c.c., of the standard $AgNO_3$ were precipitated as AgCN by the alkali cyanide in 25 c.c. of the solution.

Thus, 250 c.c. of the KCN solution are equivalent to 224 c.c. of 0·1N.$AgNO_3$. In this reaction, 1 molecule of $AgNO_3$ is equivalent to *one-half* molecule of $(CN)_2$ (note the difference) from the equivalents employed in § 91) :

$$AgNO_3 \equiv CN.$$
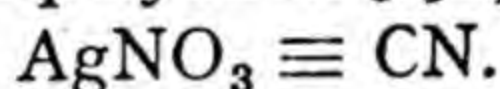
Therefore, 170 grams of $AgNO_3$ are equivalent to 26 grams of CN ; i.e. 1 litre of 0·1N.$AgNO_3$ is equivalent to 2·6 grams of CN.

Therefore, 224 c.c. of 0·1N.$AgNO_3$ are equivalent to 2·6 × 0·224, or 0·582 gram, of CN.

Thus, the percentage of CN in KCN is

$$\frac{0·582}{1·097} \times 100, \text{ or } 53·1\%.$$

SUGGESTED EXPERIMENTS ON CHAPTER VI

1. Given decinormal silver nitrate solution determine the percentage of chlorine in potassium chloride.

2. You are provided with decinormal silver nitrate solution, and are asked to determine the strength, in grams per c.c., of the bench solutions of (a) hydrochloric acid, (b) ammonium chloride, and (c) barium chloride.

3. You are provided with 5·00 grams of an intimate mixture of sodium chloride and sodium bromide. Determine, by means of decinormal silver nitrate solution, the percentage composition of the mixture.

4. Employing a decinormal solution of silver nitrate, determine the percentage purity of the laboratory potassium cyanide.

5. You are provided with pure crystalline specimens of potassium chlorate and silver nitrate, and are required to determine the percentage of chlorine in the chlorate.

6. You are provided with decinormal silver nitrate solution and a solution of hydrochloric acid. Determine (a) the percentage of $CaCO_3$ in the sample of chalk, (b) the strength of the given solution of calcium chloride in grams per c.c.

7. Given decinormal silver nitrate and moderately strong HCl, determine the percentage of carbon dioxide in ordinary washing soda.

8. Given an accurately decinormal solution of sodium chloride, determine the percentage of silver in pure, recrystallized silver nitrate.

9. Repeat experiment 8, using a decinormal solution of ammonium thiocyanate instead of the standard sodium chloride solution, and compare your results in the two experiments.

10. Given decinormal solution of NH_4CNS and $AgNO_3$, determine (a) the percentage of sodium in sodium chloride, (b) the purity of crude sodium cyanide.

11. You are provided with solutions of sodium carbonate and hydrochloric acid, and a decinormal solution of silver nitrate. Find the number of molecules of water of crystallization in hydrated calcium nitrate.

12. You are given solid silver nitrate and potassium oxalate, and are required to find the percentage of potassium in the potassium oxalate.

CHAPTER VII

OTHER VOLUMETRIC DETERMINATIONS

There are several isolated volumetric determinations which do not admit of any general classification. They are based, not so much upon special methods, as upon particular reactions, and they must, therefore, be considered separately. Several such typical determinations are studied in this chapter.

101. THE TITANOUS CHLORIDE METHOD FOR THE DIRECT ESTIMATION OF FERRIC IRON. We have seen that ferric iron may be estimated by means of potassium permanganate (§ 37), potassium dichromate (§ 53), and iodine (§ 81). All three methods are rather cumbrous—the first two involving preliminary reduction, and the iodometric method approaching completion only at a very slow rate. By means of titanous chloride, however, it is possible to estimate ferric iron quickly and accurately. The titanous chloride solution, which is purple in colour, reduces ferric salts with extreme ease, and is itself oxidized to titanic chloride, which is colourless. The ' end-point ' of the reaction is, thus, readily detected.

The reaction, in the case of ferric chloride, is represented by the equation :

$$TiCl_3 + FeCl_3 = FeCl_2 + TiCl_4.$$

The Standardization of the Titanous Chloride Solution. Owing to the ease with which $TiCl_3$ can be oxidized by atmospheric oxygen to $TiCl_4$, the standardization, and any subsequent titrations, must be carried out in an atmosphere of hydrogen.

A bottle A fitted with a tubulure (see Fig. 5) is connected to a gas-holder B filled with hydrogen, and a burette C as shown in Fig. 5. The air is forced out of the apparatus and replaced by hydrogen from the gas-holder B. 25 c.c. of ordinary commercial $TiCl_3$ solution, together with 50 c.c. of concentrated HCl, is introduced into the bottle A ; a clear blue solution is obtained after a short time, and 1 litre of air-free distilled water is then added. The burette C is filled with the $TiCl_3$ solution by releasing the clip D, the pressure of the hydrogen being kept constant by regulating the flow of water

into the gas-holder B (this precaution must also be taken in all subsequent titrations with the TiCl₃ solution). The solution is then standardized in the following manner :

About 5 grams of ferrous ammonium sulphate are weighed accurately, dissolved in air-free distilled water, acidified with a little dilute H_2SO_4, and the solution is diluted to 250 c.c. with more air-free distilled water. 25 c.c. of this solution are transferred to a small flask, and dilute $KMnO_4$ solution is run in from a burette until a permanent pink colour is obtained ; the ferrous iron is, thus, oxidized to the ferric state. This ferric iron solution is then titrated with the TiCl₃ solution, and the experiment repeated until three concordant results are obtained. The iron equivalent of the TiCl₃ solution is then calculated, and the solution labelled 1 c.c. ≡ x grams of iron.
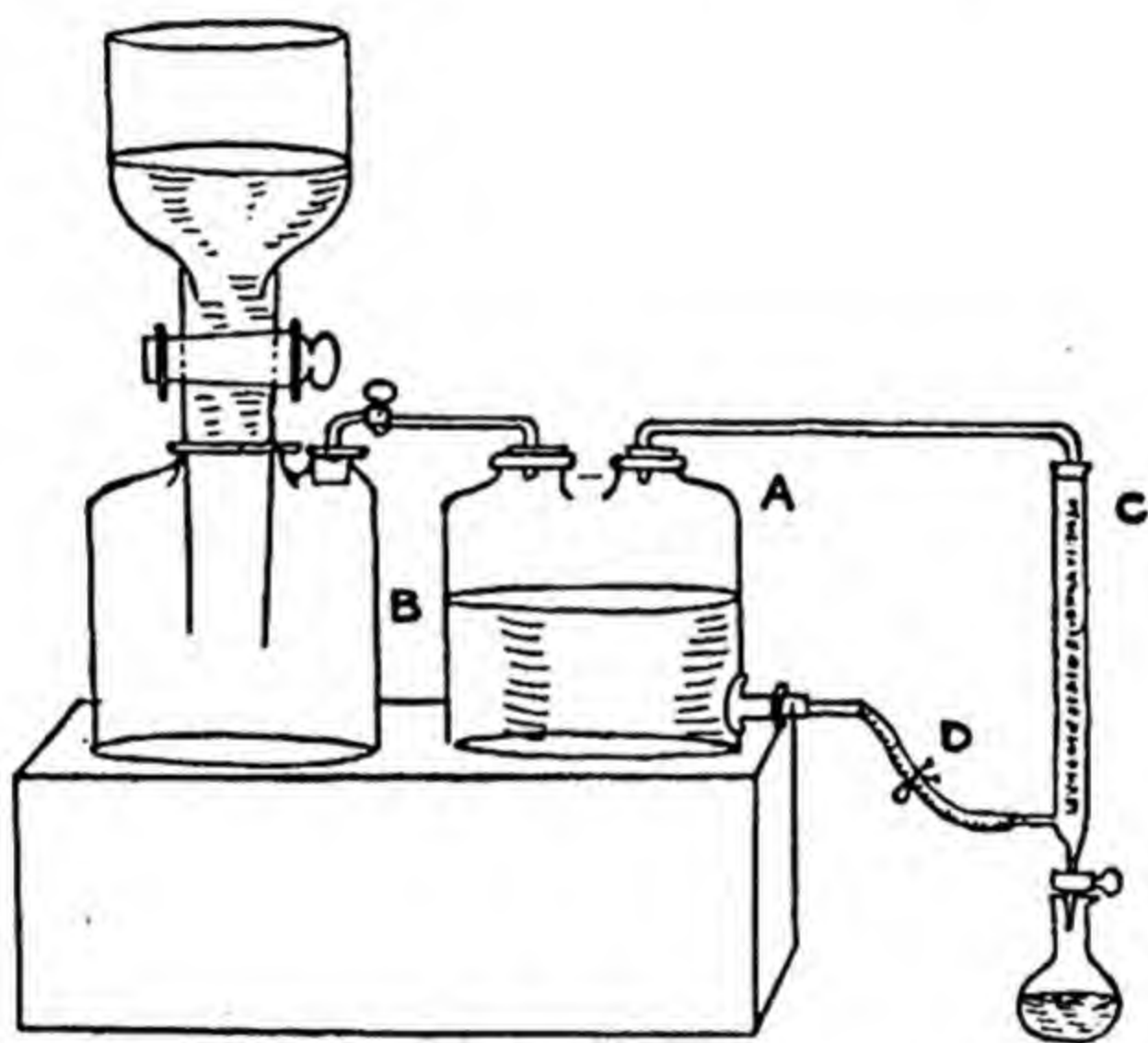
FIG. 5.

TITRATION WITH TITANOUS CHLORIDE

For example, suppose that 4·907 grams of ferrous ammonium sulphate were dissolved in air-free distilled water and diluted, after acidifying, to 250 c.c. Then the 250 c.c. of solution contain $\frac{4 \cdot 907}{7}$, or 0·701 gram of iron (see § 35).

After oxidation with dilute $KMnO_4$ solution, 25 c.c. of the iron solution required the addition of 14·0 c.c. of the TiCl₃ solution to reduce the ferric iron to the ferrous state.

Therefore, 250 c.c. of the iron solution are equivalent to 140 c.c. of the TiCl₃ solution.

Thus, 140 c.c. of the $TiCl_3$ solution are equivalent to 0·701 gram of Fe.

Therefore, 1 c.c. of the $TiCl_3$ solution is equivalent to $\frac{0·701}{140}$, or 0·005 gram, of Fe.

The $TiCl_3$ solution is thus standardized in terms of Fe and is ready for use. If the $TiCl_3$ solution is stored for any length of time, it must be restandardized as described above before making a determination, e.g. :

To Determine the Percentage of Iron in Iron Alum by Means of Standard $TiCl_3$ Solution. About 10 grams of pure, crystalline iron alum are weighed accurately, dissolved in air-free distilled water, and diluted to 250 c.c. Portions of 25 c.c of the alum solution are then titrated with the standard solution of $TiCl_3$ as described above. The determination is repeated until three concordant results are obtained, and the amount of iron is determined from the mean titration value.

For example, in an experiment, 10·33 grams of iron alum were dissolved in air-free distilled water, and diluted to 250 c.c. 25 c.c. of this solution required, as a mean of three titrations, 23·0 c.c. of a standard solution of $TiCl_3$ (1 c.c. ≡ 0·005 gram of Fe) to reduce the iron from the ferric to the ferrous condition.

Therefore, 250 c.c. of the alum solution are equivalent to 230 c.c. of the $TiCl_3$ solution ; i.e. to 230 × 0·005, or 1·15 gram of Fe.

Thus, the percentage of iron in iron alum is

$$\frac{1·15}{10·33} \times 100, \text{ or } 11·13\%.$$

102. THE CYANIDE METHOD FOR THE ESTIMATION OF COPPER. This rapid, but approximate, method of estimating copper is based upon the fact that a solution of potassium cyanide, added to an alkaline solution of a copper-ammonium salt, produced a colourless double cyanide of copper and potassium, $Cu_2(CN)_2.6KCN$. A solution containing copper may be estimated, therefore, by converting the copper into the alkaline copper-ammonium salt, and titrating directly with a standard solution of KCN, the 'end-point' being indicated by the disappearance of the blue colour of the copper-ammonium salt.

The method which gives the best results is to prepare the copper-ammonium salt by the addition of ammonium carbonate solution to the solution of the copper salt, since the

presence of free ammonia in the solution complicates the reaction.

The Standardization of the KCN Solution. (a) The KCN solution is standardized with respect to a solution of pure, electrolytic copper. The strength of the KCN solution is, thus, expressed directly as a copper equivalent. Moreover, in carrying out a titration, *the same conditions as prevailed during the standardization must be observed.* For example, the ammonium carbonate solution used in each determination with a given standard solution of KCN should be of the same strength as that used in the standardization ; and corresponding amounts of the carbonate solution must be added to each aliquot portion of the unknown copper solution.

(b) *Preparation of the Standard Copper Solution.* About 5 grams of the purest electrolytically refined copper are weighed accurately, and dissolved in about 100 c.c. of pure nitric acid mixed with its own volume of water, the solution being aided by warming on the water bath. When the copper has been completely dissolved, a little bromine water is added to oxidize the small amount of nitrous acid formed in the reaction ; the solution is then boiled to expel all the excess bromine, and the boiling is continued (care being taken to avoid loss by spitting) until most of the free nitric acid has also been removed. The solution is then allowed to cool and diluted to 1 litre with distilled water.

(c) *Preparation of the KCN Solution.* About 25 grams of pure KCN are dissolved in water and diluted to 1 litre. 25 c.c. of the standard copper solution are transferred to a small flask, and made alkaline by the addition, from a burette, of a slight excess of ammonium carbonate solution ; a deep blue coloration, due to the formation of the copper-ammonium salt, is observed, and the volume of the ammonium carbonate solution required is noted. The KCN solution is then run in from a burette until the blue colour of the solution is just discharged (*great care is necessary here*), and the titration is repeated (*using the same volume of ammonium carbonate in each case*) until three concordant results are obtained. The copper value of the cyanide is then determined from the mean titration value.

For example, suppose that the strength of the copper solution is 5·160 grams of copper per litre, and that 25 c.c. of this solution, after treatment with ammonium carbonate, required, as a mean of three titrations, 21·5 c.c. of the KCN solution to discharge the blue colour of the copper-ammonium

salt ; i.e. 860 c.c. of the KCN solution are equivalent to 1 litre of the copper solution (i.e. to 5·160 grams of Cu).

Therefore, 1 c.c. of the KCN solution is equivalent to

$$\frac{5 \cdot 160}{860}, \text{ or } 0 \cdot 006 \text{ gram, of Cu.}$$

The KCN solution is then ready for use.

The Determination of Copper in a Copper Alloy. An accurately known weight of the alloy is dissolved in strong nitric acid, the solution of the alloy being aided by gentle heat on the water bath. When the solution has been completed, a little bromine water is added to oxidize any free nitrous acid formed in the reaction ; the solution is then boiled to expel all the bromine, and the boiling is continued until most of the free acid has, also, been expelled. The solution is cooled and diluted ; and residue is filtered off, washed well with distilled water, and the combined filtrate and washings made up to a convenient volume. Aliquot portions of the copper solution are made alkaline with ammonium carbonate solution, which is run in from a burette, the volume required being noted (the carbonate solution must be of the same strength as that employed in standardizing the KCN solution, and the same volume of the carbonate solution must be added to each portion of the copper solution). Each aliquot portion is then titrated with the standard KCN solution, the 'end-point' of the titration being denoted by the disappearance of the blue colour of the copper-ammonium salt in the titrated solution.

The following results were obtained in the determination of a copper alloy by means of a standard solution of KCN (1 c.c. ≡ 0·005 gram of Cu) :

Weight of alloy taken = 3·594 grams.

Final volume of the solution of the alloy = 250 c.c.

Volume of standard KCN required to decolorize 25 c.c. of the alloy solution = 20·2 c.c.

Therefore, 250 c.c. of the alloy solution would need the addition of 202 c.c. of the standard KCN solution.

Therefore, the amount of copper in 250 c.c. of the alloy solution is 202 × 0·005, or 1·01 grams.

Thus, the percentage of copper in the alloy is

$$\frac{1 \cdot 01}{3 \cdot 594} \times 100, \text{ or } 28 \cdot 1\%.$$

103. STANDARD SODIUM SULPHIDE SOLUTION. Standard sodium sulphide solution is used in the estimation of metals

which form insoluble sulphides in alkaline solution. The two commonest determinations in which it is employed are those of Zinc and Cadmium, the sulphides of both these metals being easily precipitated in alkaline solution, viz. :

$$ZnSO_4 + Na_2S = ZnS \downarrow + Na_2SO_4,$$
$$CdSO_4 + Na_2S = CdS \downarrow + Na_2SO_4.$$
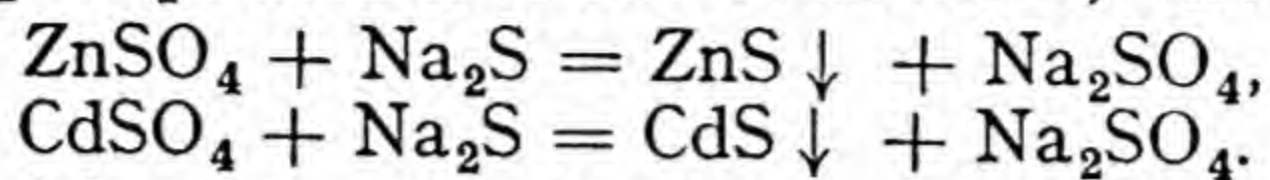
The method is of great value in the estimation of zinc in various alloys. The zinc alloy is dissolved in acid and the solution diluted to a convenient volume. Aliquot portions of the solution are then made alkaline with ammonium hydroxide solution, and titrated with a standard solution of sodium sulphide. The ' end-point ' of the determination is indicated by means of a solution of sodium nitroprusside used as an external indicator ; the indicator gives a violet coloration with alkaline sulphides though it is unaffected by free hydrogen sulphide in solution.

If, however, other metals such as copper, cadmium, etc., are present in the alloy, they must be separated from the solution of the alloy by precipitating them as sulphides before the actual estimation is begun.

Preparation of the Sodium Sulphide Solution. About 12 grams of pure stick NaOH are weighed roughly and dissolved in water and diluted to 100 c.c. 50 c.c. of this solution are then saturated with hydrogen sulphide, and sodium hydrogen sulphide is formed, viz. :

$$NaOH + H_2S = NaHS + H_2O.$$
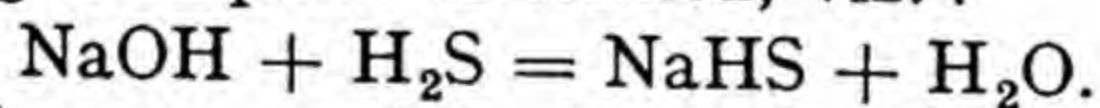
The remaining 50 c.c. of the NaOH solution are then added and sodium sulphide is formed according to the equation :

$$NaHS + NaOH = Na_2S + H_2O.$$
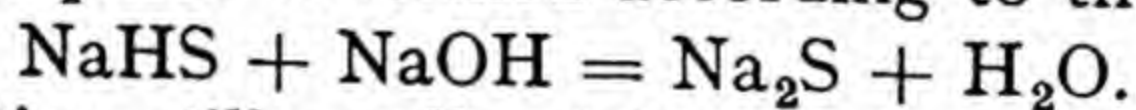
If the solution still smells of free H_2S a little more NaOH solution is added until there is no further odour of the gas ; the solution is then diluted to 1 litre with distilled water.

Standardization of the Sodium Sulphide Solution. The sodium sulphide solution is then standardized by means of a solution of pure zinc. About 1 gram of pure zinc is weighed accurately and dissolved in hot, dilute sulphuric acid (a large excess of acid must be avoided) ; the solution is then cooled, and diluted to 250 c.c. with distilled water. Aliquot portions of this solution are then titrated with the sodium sulphide solution ; several drops of sodium nitroprusside solution are placed on a white tile, and, at frequent intervals, a drop of the reacting solutions is added to a drop of the indicator by means of a glass rod, the ' end-point ' of the titration being

indicated by a distinct violet coloration. Three concordant results are obtained, and the strength of the sodium sulphide solution expressed in terms of zinc.

For example, suppose that 1·125 grams of pure zinc were dissolved in hot, dilute, sulphuric acid and diluted to 250 c.c., and that, as a mean of three titrations, 25 c.c. of this solution required the addition of 22·5 c.c. of the sodium sulphide solution to give the violet coloration with sodium nitro-prusside.

Then, 250 c.c. of the zinc solution would need 225 c.c. of the sodium sulphide solution.

Therefore, 225 c.c. of the sodium sulphide solution are equivalent to 1·125 grams of zinc ; i.e. 1 c.c. of the sodium sulphide solution is equivalent to *0·005 gram of zinc*.

104. TO DETERMINE THE PERCENTAGE OF ZINC IN A SPECIMEN OF ZINC BLENDE BY MEANS OF STANDARD SODIUM SULPHIDE SOLUTION. An accurately known weight of the zinc blende is dissolved in aqua regia, and diluted. The solution is then tested qualitatively for traces of copper, cadmium, and lead, and, if these are present, they are precipitated as sulphides by means of H_2S ; the solution is then freed from free H_2S by boiling, and it is then cooled and diluted to a convenient volume.* Aliquot portions of this solution are then titrated with freshly-standardized sodium sulphide solution, using sodium nitroprusside as an external indicator (as described in § 103). The amount of zinc in the solution is then calculated from the mean titration value.

For example, 1·703 grams of zinc blende were dissolved in aqua regia, freed from copper and cadmium by precipitation as sulphides, and diluted to 500 c.c. As a mean of three titrations, it was found that 50 c.c. of this solution required the addition of 21·8 c.c. of standard sodium sulphide solution (1 c.c. $\equiv$ 0·005 gram of Zn) to produce the violet coloration with sodium nitroprusside.

Therefore, 500 c.c. of the solution would require 218 c.c. of the Na_2S solution ; i.e. 500 c.c. of the zinc blende solution are equivalent to 218 × 0·005, or 1·09 grams, of zinc.

Therefore, the percentage of zinc in the sample of zinc blende is

$$\frac{1·09}{1·703} \times 100, \text{ or } 64·0\%.$$

105. THE ESTIMATION OF CADMIUM SALTS BY MEANS OF STANDARD SODIUM SULPHIDE. An accurately known weight

* The solution must first be made alkaline with ammonium hydroxide.

of the cadmium salt is dissolved in water and diluted to a convenient volume (if the cadmium salt is insoluble in water it is dissolved in strong nitric acid, the solution is made alkaline by the addition of ammonium hydroxide, and diluted to a suitable volume). Aliquot portions of the solution are then titrated with a standard solution of sodium sulphide, using a solution of sodium nitroprusside as the indicator as described in § 103.

The sodium sulphide solution is still standardized with respect to pure zinc, and the strength is then expressed in terms of cadmium.

For example, in an experiment to estimate the percentage of cadmium in a soluble cadmium salt, a standard solution of sodium sulphide (1 c.c. $\equiv$ 0·005 gram of Zn) was employed.

4·219 grams of a soluble cadmium salt were dissolved in water and diluted to 250 c.c. As a mean of three titrations, it was found that 25 c.c. of this solution required the addition of 21·5 c.c. of the standard Na$_2$S solution to produce the colour change with sodium nitroprusside. Thus, 250 c.c. of the cadmium solution are equivalent to 218 c.c. of the Na$_2$S solution, i.e. to 215 × 0·005, or 1·075 grams, of zinc.

Now, $$Zn \equiv Cd.$$

Therefore, 65·37 grams of Zn are equivalent to 112·4 grams of Cd.

Therefore, 1·075 grams of Zn are equivalent to $\frac{112·4}{65·37} \times 1·075$, or 1·848 grams, of Cd.

Thus, the percentage of cadmium in the cadmium salt is

$$\frac{1·848}{4·219} \times 100, \text{ or } 43·8\%.$$

106. THE POTASSIUM FERROCYANIDE METHOD FOR THE ESTIMATION OF ZINC. The method is based upon the fact that, when potassium ferrocyanide is allowed to react with a solution of a zinc salt, at a temperature of about 90° C., a double cyanide of potassium and zinc is formed. The 'end-point' of the reaction is determined by means of uranyl acetate solution as an external indicator (see below). The reaction may be represented by the equation :

$$2K_4Fe(CN)_6 + 3ZnCl_2 = 3[2KCN.Zn(CN)_2] + 2FeCl_2 + 2KCl.$$
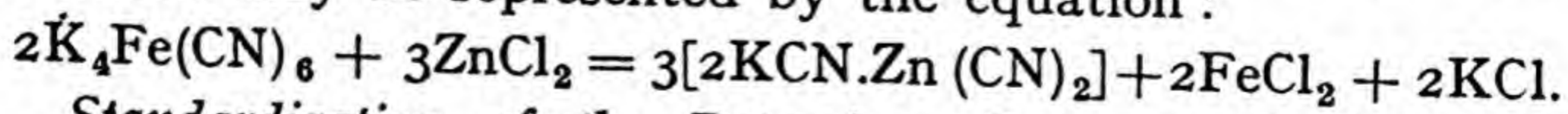
Standardization of the Potassium Ferrocyanide Solution. About 35 grams of pure potassium ferrocyanide are weighed roughly, dissolved in water, and diluted to 1 litre. A standard

zinc solution is then prepared in exactly the same way as described in § 103 for the standardization of sodium sulphide solution. Aliquot portions of the zinc solution are then warmed to about 95° C., and titrated with the ferrocyanide solution, using a solution of uranyl acetate as an external indicator ; several drops of the indicator solution are placed on a white tile, and, at frequent intervals during the titration, a drop of the reacting solutions is withdrawn on the end of a glass rod and added to a drop of the indicator ; the 'end-point' of the titration is indicated by the first production of the brown colour of uranyl ferrocyanide.

As the reaction is rather slow, the titration must be carried out slowly in order to allow sufficient time for the formation of the double cyanide to be completed. The strength of the ferrocyanide solution is then expressed in terms of metallic zinc.

For example, about 35 grams of pure potassium ferro-cyanide were dissolved in water and diluted to 1 litre. 1·025 grams of pure zinc-foil were dissolved in dilute, hot sulphuric acid, cooled, and diluted to 250 c.c., and it was found, as a mean of three titrations, that 25 c.c. of the zinc solution were equivalent to 20·5 c.c of the ferrocyanide solution, using uranyl acetate as the indicator.

Then, 250 c.c. of the zinc solution are equivalent to 205 c.c. of $K_4Fe(CN)_6$.

Thus, 205 c.c. of $K_4Fe(CN)_6$ are equivalent to 1·025 grams of zinc ; i.e. 1 c.c. of the ferrocyanide solution $\equiv \dfrac{1·025}{205}$, or 0·005 grams, of Zn.

To Determine the Amount of Zinc in a Specimen of Zinc Blende. A known weight of the zinc blende is dissolved and made up to suitable strength exactly as described in § 104. Aliquot portions of the solution are then titrated with the standard solution of potassium ferrocyanide, using uranyl acetate as an external indicator, in the manner described above. The amount of zinc is then estimated from the mean titration value.

As a check on the determination carried out in § 104, 50 c.c. of the final zinc solution (equivalent to 1·703 grams of zinc blende per 500 c.c.) were titrated with standard potassium ferrocyanide solution (1 c.c. $\equiv$ 0·005 gram of Zn), and it was found that a mean volume of 21·8 c.c. of the ferrocyanide solution was needed to effect the colour change with uranyl acetate.

Therefore, 500 c.c. of the solution are equivalent to 218×0.005, or 1.09 grams, of zinc.

Thus, the percentage of zinc in the sample of zinc blende is

$$\frac{1.09}{1.703} \times 100, \text{ or } 64.0\%.$$

Thus, the estimation of the zinc blende gives identical results with each method.

107. THE SODIUM SULPHITE METHOD FOR THE DETERMINATION OF ALDEHYDES. It is a characteristic property of aldehydes that they combine with sodium bisulphite to form additive crystalline compounds, viz. :

$$CH_3CHO + NaHSO_3 \equiv CH_3HC{\Large<}^{ONa}_{SO_2OH}$$
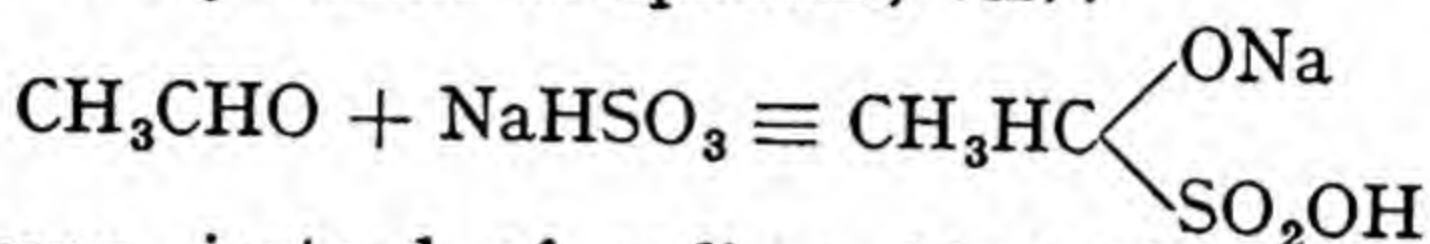
If, however, instead of sodium bisulphite, the normal sodium sulphite is used, the same additive aldehyde-bisulphite compound is formed and an equivalent amount of NaOH is liberated, viz. :

$$H_2O + CH_3CHO + Na_2SO_3 = CH_3HC{\Large<}^{ONa}_{SO_2OH} + NaOH.$$
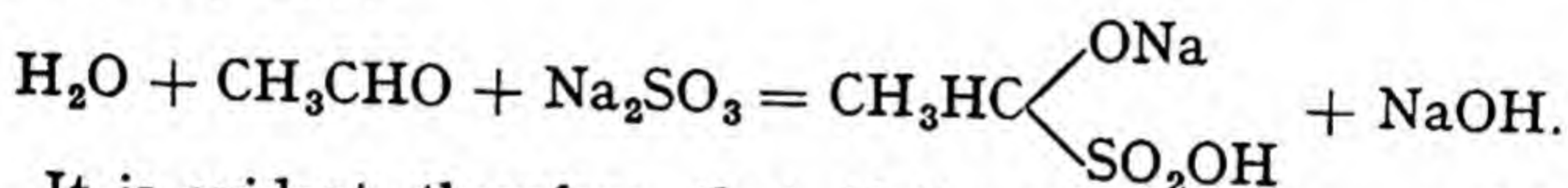
It is evident, therefore, that, if the solution is neutral in the first place, we have an indirect means of estimating the aldehyde by titration of the liberated NaOH with standard acid. In the actual determination, if the solution of aldehyde is fairly strong, it must be diluted to a suitable strength.

The Preparation of the Sodium Sulphite Solution. About 25 grams of pure, hydrated sodium sulphite, $Na_2SO_3.7H_2O$, are dissolved in 100 c.c. of distilled water. The solution is then made exactly neutral to phenolphthalein by the addition, if necessary, of very dilute NaOH solution from a burette. The solution is then ready for use ; e.g. :

To Determine the Strength of an Acetaldehyde Solution. 25 c.c. of the acetaldehyde solution are transferred to a small flask and immersed in a freezing mixture. 25 c.c. of the freshly prepared sodium sulphite are then added slowly, about 5 c.c. at a time, and the mixture is allowed to stand for about fifteen minutes. The solution is then titrated with decinormal sulphuric acid, using litmus solution as the indicator ; the solution must be kept at 0° C. during the titration, which must be carried out very slowly in order to avoid the decomposition of the aldehyde-bisulphite compound. Three concordant results are obtained, and the amount

10

is determined from the mean titration value, employing the equivalents :

$$H_2SO_4 \equiv 2NaOH \equiv 2CH_3CHO.$$
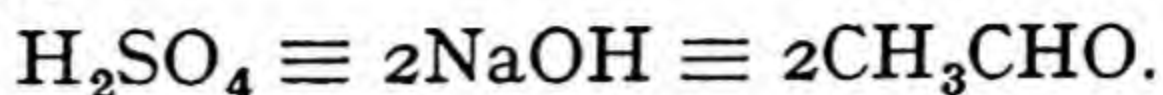
Thus, 49·0 grams of H_2SO_4 are equivalent to 44·0 grams of CH_3CHO ; i.e. 1 litre of 0·1N.H_2SO_4 is equivalent to 4·40 grams of CH_3CHO.

For example, in the estimation of a solution of acetaldehyde 25 c.c. of the solution were diluted to 250 c.c. after treatment with excess of neutral sodium sulphite solution. It was found that, as a mean of three titrations, 25 c.c. of the diluted solution required the addition of 23·5 c.c. of 0·1N.H_2SO_4 to neutralize the liberated NaOH at 0° C.

Therefore, 25 c.c. of the original solution (250 c.c. of diluted solution) would require 235 c.c. of 0·1N.H_2SO_4.

Then, since 1 litre of 0·1N.H_2SO_4 is equivalent to 4·40 grams of CH_3CHO, 235 c.c. of 0·1N.H_2SO_4 are equivalent to 4·4 × 0·235, or 1·034 grams, of CH_3CHO.

Thus, 1 litre of the aldehyde solution contains 40 × 1·034, or *41·36 grams. of CH₃CHO.*

108. The Use of a Standard Solution of Potassium Bromide and Bromate. The potassium bromide and the potassium bromate must be in the molecular proportions 5KBr : $KBrO_3$. The standard solution is best prepared by adding bromine carefully to a saturated solution of caustic potash until no more bromine is absorbed. If crystals of the bromate or the bromide are formed during this operation the solution must be diluted in order to dissolve them, and a little more bromine is added. Bromine water is then added until the solution is only just alkaline.

The bromide-bromate solution is then ready for use in estimating *aniline in aqueous solution.*

Before use, the bromide-bromate solution is standardized by means of a known quantity of aniline in the form of aniline hydrochloride. The most convenient strength solution to employ is one, 1 c.c. of which is equivalent to 0·025 gram of aniline.

The Standardization of the Bromide-bromate Solution. 1 gram of aniline is weighed accurately and dissolved in 40 c.c. of water to which 10 c.c. of concentrated HCl have been added. This solution of aniline hydrochloride is then titrated with the bromide-bromate solution ; the solution is run in a drop at a time, and the mixture is well shaken after each addition. A white precipitate of tribromaniline

is formed and, at the start, the supernatant liquid is clear and colourless. The titration is continued until this supernatant liquid is tinged a faint yellow with the excess bromine. The reactions occurring in the reaction are as follows :

(i) The free HCl in the solution liberates hydrobromic and bromic acids from the bromide-bromate mixture :

$$5KBr + KBrO_3 + 6HCl = 5HBr + HBrO_3 + 6KCl.$$
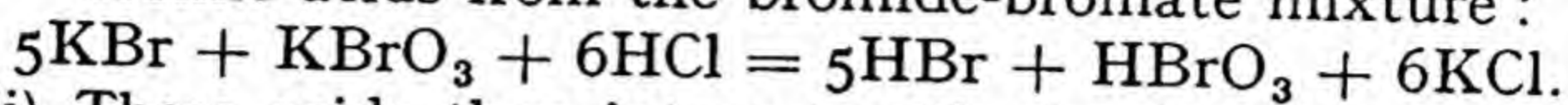
(ii) These acids then interact with the formation of free bromine :

$$5HBr + HBrO_3 = 3Br_2 + 3H_2O.$$
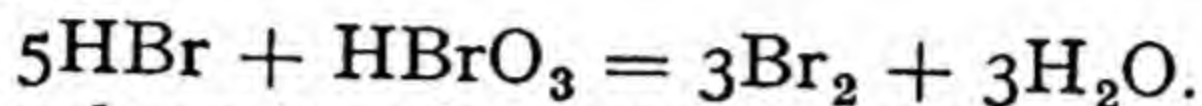
(iii) The free bromine then attacks the aniline forming the insoluble aniline-bromine derivative :

$$C_6H_5NH_2 + 3Br_2 = C_6H_2Br_3NH_2 + 3HBr.$$
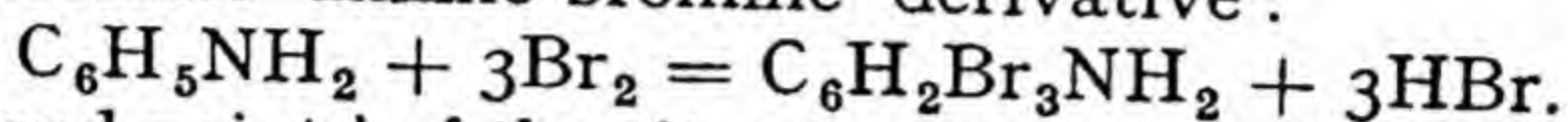
The 'end-point' of the titration is thus indicated when the aniline has all been converted to the bromine derivative, and the supernatant liquid then becomes yellow, owing to the presence of free bromine in the solution.

Three concordant results are obtained and the bromide-bromate solution is standardized with reference to aniline. For example, suppose that the solution of 1 gram of aniline required the addition of 40 c.c. of the bromide-bromate solution to produce the faint yellow colour in the supernatant liquid, then

1 c.c. of the bromide-bromate solution is equivalent to $\frac{1 \cdot 0}{40}$, or 0·025 gram, of aniline.

For an account of a determination of a solution of aniline with standard bromide-bromate solution see § 134 : the determination of the solubility of aniline in aqueous solution.

109. THE DETERMINATION OF PHOSPHATES BY MEANS OF STANDARD URANIUM SOLUTION. The standard uranium solution employed may be prepared from either uranyl acetate or uranyl nitrate, though where the latter salt is used a little sodium acetate must also be present to prevent the formation of free nitric acid.

Uranium forms a series of salts containing the divalent uranyl group, $(U\bar{\bar{O}}_2)$, which may be regarded as analogous to the bismuthyl salts, e.g. bismuthyl nitrate, $(BiO)NO_3.H_2O$; or to the antimonyl salts, e.g. potassium-antimony tartrate, $(SbO)K(C_4H_6O_6)$. These uranyl salts react with ortho-phosphates, in the presence of acetic acid, forming a yellow precipitate of the corresponding uranyl phosphate, viz. :

With uranyl nitrate,

$$(UO_2)(NO_3)_2 + Na_2HPO_4 = 2NaNO_3 + (UO_2)HPO_4.$$
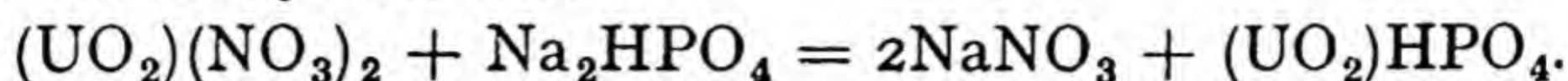
Free HNO_3 is formed in this reaction unless a little sodium acetate be present.

With uranyl acetate—

$$(UO_2)(CH_3COO)_2 + Na_2HPO_4 = 2CH_3COONa + (UO_2)HPO_4$$
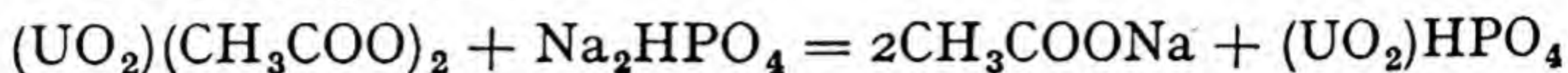
A solution of an orthophosphate may be estimated, therefore by titration with a standard solution of either uranyl acetate or uranyl nitrate. The 'end-point' of the titration is indicated by means of dilute potassium ferrocyanide solution, used as an external indicator in the usual way, which gives a brown coloration of uranyl ferrocyanide when the slightest trace of excess uranyl solution is present in the reacting solutions.

The Standardization of the Uranium Solution. (a) *Uranyl Acetate.* About 32 grams of pure uranium acetate, $(UO_2)(CH_2COO)_2.2H_2O$, are dissolved in water, 50 c.c. of glacial acetic acid are added, and the solution is diluted to 1 litre.

(b) *Uranyl Nitrate.*—About 37 grams of pure uranyl nitrate are dissolved in water, 50 c.c. of glacial acetic acid are added, and the solution diluted to 1 litre.

The uranyl solution (prepared in one of the above ways) is then standardized, in terms of P_2O_5, by means of pure hydrogen-sodium-ammonium phosphate (microcosmic salt), $NaNH_4HPO_4.4H_2O$, at a temperature of about $90°$ C.

About 3·5 grams of the pure, crystalline microcosmic salt are dissolved in water and diluted to 250 c.c. 25 c.c. of this solution are transferred to a small flask and titrated, at a temperature not below $90°$ C., with uranyl acetate solution prepared as above (if uranyl nitrate solution is employed, 5 c.c. of a 10% solution of sodium acetate, and a few drops of glacial acetic acid, must be added to each 25 c.c. of the phosphate solution, to prevent the formation of free nitric acid). The 'end-point' of the titration is indicated by the formation of a brown coloration, with a dilute solution of potassium ferrocyanide used as an external indicator. After this preliminary titration, three concordant results are obtained, and the strength of the uranyl solution is expressed in terms of P_2O_5.

For example, suppose that the phosphate solution contained 3·680 grams of crystalline microcosmic salt in 250 c.c.

Then, $2NaNH_4HPO_4.4H_2O \equiv P_2O_5.$

Therefore, 418 grams of $NaNH_4HPO_4.4H_2O$ are equivalent to 142 grams of P_2O_5.

Then, 3·680 grams of the salt are equivalent to $\frac{142}{418} \times 3\cdot680$, or 1·250 grams, of P_2O_5.

Thus, 1 litre of the phosphate solution is equivalent to $4 \times 1\cdot25$, or *5·00 grams, of P_2O_5.*

Suppose, further, that 25 c.c. of this phosphate solution required the addition of 24·5 c.c. of the uranyl acetate solution to effect the colour change with potassium ferrocyanide.

Thus, if each 24·5 c.c. of the uranyl solution be diluted to 25 c.c., it will be equivalent to the phosphate solution.

Consequently, $40 \times 24\cdot5$, or 980 c.c., of the solution must be diluted to 1 litre so that 1 c.c. of the uranyl solution shall be equivalent to 0·005 gram of P_2O_5.

N.B.—The uranyl solution may also be standardized by employing a solution of pure, calcium phosphate, $Ca_3(PO_4)_2$, in dilute HCl; but, since the purest form of commercial calcium phosphate contains certain impurities, this method is not accurate unless the percentage purity of the calcium phosphate is first determined by gravimetric methods. In consequence, it is much more convenient to standardize the uranyl solution by means of microcosmic salt, which can be easily obtained in a state of purity.

110. THE DETERMINATION OF P_2O_5 IN BONE ASH BY MEANS OF STANDARD URANIUM SOLUTION. About 1 or 2 grams of bone ash (which has been dried in the steam oven) are weighed accurately and dissolved in the least possible quantity of concentrated HCl; the solution is then diluted to 200 c.c. 50 c.c. of this solution are transferred to a small flask, about 5 c.c. of a 10% solution of sodium acetate and a few drops of glacial acetic acid are added, and the solution is heated until it begins to boil. It is then titrated, at a temperature not below 90° C., with the standard solution of uranium (prepared as described in § 109), using potassium ferrocyanide as an external indicator. Three concordant results are obtained and the amount of P_2O_5 is calculated from the mean titration value.

For example, in a determination, 1·50 grams of dry bone ash were dissolved in concentrated HCl, and the solution was diluted to 200 c.c. As a mean of three titrations, it was found that 50 c.c. of the bone ash solution required 25·5 c.c. of a standard uranium solution (1 c.c. ≡ 0·005 gram of P_2O_5) to effect the colour change with potassium ferrocyanide.

Thus 200 c.c. of the solution would require $4 \times 25 \cdot 5$, or 102 c.c., of the standard uranium solution; i.e. 200 c.c. of the solution are equivalent to $102 \times 0 \cdot 005$, or $0 \cdot 51$ gram, of P_2O_5.

Therefore, $1 \cdot 50$ grams of bone ash contain $0 \cdot 51$ gram of P_2O_5.

Thus, the percentage of P_2O_5 in the sample of bone ash is

$$\frac{0 \cdot 51}{1 \cdot 50} \times 100, \text{ or } 34\%, P_2O_5.$$

III. The Standard Soap Solution Method for Determining the Hardness of Water. Although Hehner's method of estimating the hardness of water gives excellent results (see § 31), the standard soap solution method is widely employed. For this purpose pure Castile soap which consists of the alkali salt of oleic acid, is employed, and the method is based upon the fact that the soap precipitates the calcium and magnesium salts, present in the water, as insoluble oleates; e.g.:

$$2C_{17}H_{33}COONa + CaSO_4 = (C_{17}H_{33}COO)_2Ca + Na_2SO_4.$$
sodium oleate $\qquad\qquad$ calcium oleate

The soap solution is made to such a strength that 1 c.c. of the solution will precipitate exactly 1 milligram of $CaCO_3$ as oleate; then, by titrating 70 c.c. of water, the hardness can be found directly in grains per gallon (parts per 70,000).

About 2 grams of pure Castile soap are dissolved in 200 c.c. of dilute alcohol (1 volume of alcohol to 2 volumes of water). The solution is thoroughly shaken until all the soap has dissolved, and the soap solution is then standardized.

Standardization of the Soap Solution. 0·5 gram of pure Iceland Spar is weighed accurately and dissolved in dilute HCl in a beaker covered with a clock-glass; the solution is evaporated to dryness on the water bath, and the residue is dissolved in distilled water and again evaporated to dryness to remove all traces of HCl. The residual $CaCl_2$ is finally dissolved in distilled water and diluted to as many cubic centimetres as milligrams of $CaCO_3$ were taken (in this case 500). Thus, 1 c.c. of the solution is equivalent to 1 milligram of $CaCO_3$.

20 c.c. of this solution are transferred to a small flask and diluted to 70 c.c. (the volume of water used in a determination) with distilled water. The solution is then titrated with the soap solution; 1 c.c. of the soap solution is added at a time, and the mixture is well shaken after each addition until a temporary lather is obtained; the soap solution is then

added 1 drop at a time, well shaken after each addition, until a lather is obtained which will persist for at least two minutes. Three concordant results are obtained. We then calculate the volume of water which must be added to the soap solution so that 21 c.c. will produce a permanent lather with 20 c.c. of the *original* CaCl$_2$ solution (the extra 1 c.c. is the amount of soap solution required to produce a permanent lather with the 70 c.c. of distilled water).

For example, suppose that, as a mean of three determinations, 20 c.c. of the CaCl$_2$ solution (i.e. 20 milligrams of CaCO$_3$) require 18·0 c.c. of the soap solution to produce a permanent lather.

Then, (21 — 18), or 3 c.c., of distilled water must be added to each 18 c.c. of the soap solution to make it equivalent to the CaCl$_2$ solution. The calculated amount of distilled water is then added to a convenient volume of the soap solution, which is then labelled 1 c.c. ≡ 0·001 gram of CaCO$_3$, or its equivalent of MgCO$_3$.

TO DETERMINE THE HARDNESS OF TAP-WATER

Method. The TOTAL HARDNESS is first determined by precipitating all the calcium and magnesium salts with the standard soap solution. Then, by boiling the solution to precipitate the temporary hardness as carbonate, and titrating the resulting solution with the soap solution, the PERMANENT HARDNESS is determined. The TEMPORARY HARDNESS is then obtained by difference.

(a) *To Determine the Total Hardness of the Tap-water.* 70 c.c. of the tap-water are titrated with the standard soap solution, as described above; three concordant results are obtained, and the number of c.c. of soap solution required to produce the permanent lather will give the total hardness of the tap-water directly in grains per gallon (parts per 70,000).

(b) *To Determine the Permanent Hardness of the Tap-water.* 250 c.c. of the tap-water are boiled until the volume has decreased to about 100 c.c. The temporary hardness is, thus, completely precipitated, viz. :

$$Ca(HCO_3)_2 = CaCO_3 \downarrow + CO_2 + H_2O.$$
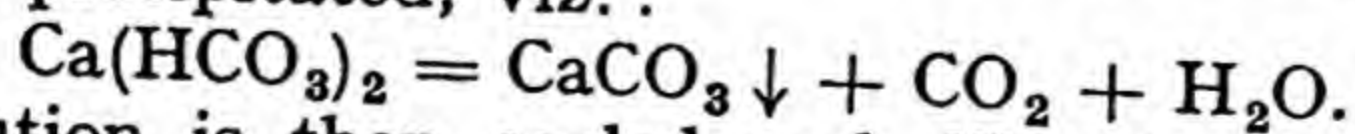
The solution is then cooled and diluted to the original volume with distilled water. Portions of 70 c.c. are titrated with the standard soap solution exactly the same as before, and the number of c.c. of soap solution required to produce

the lather gives the permanent hardness of the tap-water directly in grains per gallon.

(c) *To Determine the Temporary Hardness of the Tap-water.* The difference between the total hardness and the permanent hardness will represent the temporary hardness.

For example, in a determination of the hardness of a specimen of tap-water it was found that 70 c.c. required a mean volume of 23·5 c.c. of soap solution (1 c.c. $\equiv$ 0·001 gram of $CaCO_3$) to produce a permanent lather ; i.e. :

The TOTAL HARDNESS is 23·5 grains of $CaCO_3$ (or its equivalent of $MgCO_3$) per gallon.

After precipitating the temporary hardness as described above, it was found that 70 c.c. of the water required a mean volume of 8·1 c.c. of the soap solution to produce a permanent lather ; i.e. :

The PERMANENT HARDNESS is 8·1 grains of $CaCO_3$ (or its equivalent of $MgCO_3$) per gallon.

Therefore, the TEMPORARY HARDNESS is (23·5 — 8·1), or 15·4 grains, of $CaCO_3$ (or its equivalent of $MgCO_3$) per gallon.

SUGGESTED EXPERIMENTS ON CHAPTER VII

1. You are provided with commercial titanous chloride solution, solid ferrous ammonium sulphate, and a solution of potassium permanganate. Prepare a standard solution of titanous chloride, and store it in an atmosphere of hydrogen.

2. By means of the standard titanous chloride prepared above, determine the percentage of iron in the given specimen of anhyrdous ferric chloride.

3. You are provided with pure, electrolytically-refined copper, and solid potassium cyanide. Prepare a standard solution of KCN, 1 c.c. of which should be equivalent to 0·005 gram of copper.

4. By means of the standard KCN solution prepared above determine the percentage of copper in crystalline cupric chloride.

5. You are provided with pure sodium sulphide crystals, $Na_2S.9H_2O$, pure zinc-foil, and dilute sulphuric acid. Prepare a standard solution of sodium sulphide so that 1 c.c. of the solution will be equivalent to 0·005 gram of zinc.

6. By means of the standard solution of sodium sulphide prepared above, determine the percentage of zinc in hydrated zinc sulphate.

7. You are provided with potassium ferrocyanide, pure zinc-foil, and dilute sulphuric acid, and are required to prepare a standard solution of potassium ferrocyanide, 1 c.c. of which should be equivalent to 0·005 gram of zinc.

8. By means of the standard solution of potassium ferrocyanide prepared above, determine the percentage of zinc sulphate, and compare your result with that obtained in Experiment 6.

9. You are provided with pure, crystalline sodium sulphite, $Na_2SO_3.7H_2O$, and have to determine the strength of the given solution of acetaldehyde in grams per c.c.

10. You are provided with pure uranyl nitrate, $UO_2(NO_3)_2.2H_2O$, and pure crystalline sodium ammonium hydrogen phosphate, $NaNH_4HPO_4.4H_2O$; sodium acetate and glacial acetic acid are also provided. You are asked to prepare a standard solution of uranyl nitrate, 1 c.c. of which should be equivalent to 0·005 gram of P_2O_5.

11. By means of the standard uranyl nitrate solution prepared above, find the percentage purity of the laboratory phosphorous pentoxide.

12. You are provided with pure sodium oleate, alcohol, Iceland spar, and strong HCl. Prepare a standard sodium oleate solution so that 1 c.c. of the solution will be equivalent to 1 milligram of $CaCO_3$.

13. By means of the standard sodium oleate solution prepared above, determine (a) the permanent hardness, (b) the temporary hardness of tap-water.

14. You are provided with aniline hydrochloride, and a mixture of potassium bromide and bromate in the molecular proportions $5KBr : KBrO_3$. You are required to determine the number of atoms of bromine in the aniline derivative formed by adding a solution of the bromide-bromate mixture to a solution of the aniline hydrochloride.

CHAPTER VIII

DETERMINATIONS INVOLVING MORE THAN ONE METHOD OF VOLUMETRIC ANALYSIS

112. We have seen that mixtures containing two constituents of the same chemical type can be estimated volumetrically by basing the calculation on the difference in chemical equivalents (see §§ 24, 25, 26, and 90).

In many cases of mixtures of two, or more, substances of different chemical types, it is possible to determine the mixture by the application of more than one method of volumetric analysis. For example, a mixture of a halide and an alkali (or acid) could be determined by estimating the alkali (or acid) with standard acid (or alkali), and then estimating the halide, in neutral solution, with standard silver nitrate solution. Other examples of this type of volumetric determination are given below.

113. TO ESTIMATE A MIXTURE OF SULPHURIC AND OXALIC ACIDS. The method of determination is as follows:

(a) Titrate aliquot portions of the mixture (diluted if necessary), at a temperature of 60° C, with standard potassium permanganate (see § 35 (b)), and calculate the amount of oxalic acid from the mean titration value.

(b) Further aliquot portions of the solution are then titrated with standard NaOH. The mean titration value thus obtained represents the total acidity of the solution. The amount of sulphuric acid is then obtained by difference.

For example, 25 c.c. of a solution containing a mixture of sulphuric and oxalic acids required a mean titration of 18·3 c.c. of o·1N.KMnO$_4$ to oxidize all the oxalic acid, and a mean value of 48·3 c.c. of o·1N.NaOH to neutralize the total acid: i.e. 25 c.c. of the solution contain the equivalent of (48·3 − 18·3), or 30·0 c.c., of o·1N.H$_2$SO$_4$.

Thus, 1 litre of the mixture is equivalent to 40 × 18·3, or 732, c.c. of o·1N.KMnO$_4$; i.e. to the same volume of o·1N. oxalic acid.

Then, since 1 litre of o·1N. oxalic acid contains 4·5 grams of anhydrous oxalic acid, 732 c.c. of o·1N. oxalic acid would contain 4·5 × 0·732, or *3·29 grams, of anhydrous oxalic acid.*

And 1 litre of the solution contains the equivalent of 40 × 30, or 1200 c.c., of $0.1N.H_2SO_4$; i.e. 4·9 × 1·2, or 5·88 *grams, of* H_2SO_4.

Thus,

1 litre of the acid solution contains $\begin{cases} 3\text{·}29 \text{ grams of } (COOH)_2, \\ 5\text{·}88 \text{ grams of } H_2SO_4. \end{cases}$

114. TO DETERMINE A SOLUTION CONTAINING AN INORGANIC HALIDE AND FREE ACID. The free acid is estimated by means of standard NaOH, and the halide, in neutral solution, by means of standard silver nitrate. When, however, HCl is the acid in the solution, it will also be precipitated as AgCl by titration with silver nitrate; so that, in this case, the total chlorine has to be estimated, and the amount of halide determined by difference.

(a) *To Estimate a Solution containing a Mixture of NaCl and HCl.* (i) Aliquot portions of the solution are titrated with standard alkali, and the amount of HCl deduced from the mean titration value. Suppose this mean volume to be n_1 c.c.

(ii) To aliquot portions of the solution add n_1 c.c. of standard alkali (without the indicator); the reason for this is, of course, that the estimation of the chlorine by standard silver nitrate must be carried out in neutral solution. The *total chlorine* is then determined by titration with standard silver nitrate (see § 87), using potassium chromate as the indicator. Suppose the mean titration value to be n_2 c.c.

Then, the amount of NaCl in each aliquot portion of the solution is equivalent to $(n_2 - n_1)$ c.c. of standard silver nitrate.

For example, in an experiment, 25 c.c. of a solution containing NaCl and HCl required a mean volume of 17·2 c.c. of $0.1N.NaOH$ to neutralize the HCl, and 47·7 c.c. of $0.1N.AgNO_3$ to precipitate all the chlorine as AgCl.

(i) *Calculation of the HCl.* 1 litre of the solution is equivalent to 40 × 17·2, or 688 c.c., of $0.1N.NaOH$.

Then, since 1 litre of $0.1N.NaOH$ is equivalent to 3·65 grams of HCl, 688 c.c. of $0.1N.NaOH$ will be equivalent to 3·65 × 0·688, or 2·51 *grams, of HCl.*

(ii) *Calculation of the NaCl.* 1 litre of the solution is equivalent to 40 × 47·7, or 1908 c.c., of $0.1N.AgNO_3$, and, of this amount, 688 c.c. are equivalent to the HCl; therefore (1908 − 688), or 1220 c.c., of $0.1N.AgNO_3$ are equivalent to the NaCl.

Now, 1 litre of o·1N.AgNO$_3$ is equivalent to 5·85 grams of NaCl. Therefore 1·22 litres of o·1N.AgNO$_3$ are equivalent to 5·85 × 1·22, or *7·14 grams, of NaCl.*

Thus,

1 litre of the solution contains $\begin{cases} \textit{2·51 grams of HCl,} \\ \textit{7·14 grams of NaCl.} \end{cases}$

(b) *To Estimate a Solution containing a Mixture of NaCl and HNO$_3$.* The procedure is exactly the same as in the previous determination. (i) Aliquot portions of the solution are titrated with standard NaOH, and the amount of HNO$_3$ calculated from the mean titration value (n_1 c.c.). (ii) Aliquot portions of the solution are then carefully neutralized by the addition of n_1 c.c. of the standard NaOH (without the indicator), and the NaCl determined by titration with standard silver nitrate solution.

Let the mean titration value be n_2 c.c.

Then, the amount of HNO$_3$ in the solution is equivalent to n_1 c.c. of standard NaOH, and the NaCl is equivalent to n_2 c.c. of standard AgNO$_3$.

115. To Determine a Solution containing an Inorganic Halide and an Alkali. The method is similar to that for the determination of a mixture of a halide and an acid.

(a) Aliquot portions of the solution are titrated with standard acid and the amount of alkali determined from the mean titration value (n_1 c.c.).

(b) Aliquot portions of the solution are then neutralized by the addition of n_1 c.c. of standard acid (without the indicator), and the halide is determined from the mean titration value obtained with standard silver nitrate (see § 87).

For example, 25 c.c. of a solution containing KBr and KOH required a mean volume of 23·5 c.c. of o·1N.H$_2$SO$_4$ to neutralize the KOH, and 20·4 c.c. of o·1N.AgNO$_3$ to precipitate all the bromide as AgBr; i.e. 1 litre of the solution is equivalent to 940 c.c. of o.1N.H$_2$SO$_4$, and 816 c.c. of o·1N.AgNO$_3$.

(a) *Calculation of the KOH.* 1 litre of o·1N.H$_2$SO$_4$ is equivalent to 5·6 grams of KOH. Therefore, 940 c.c. of o·1N.H$_2$SO$_4$ are equivalent to 5·6 × 0·94, or *5·26 grams, of KOH.*

(b) *Calculation of the KBr.* 1 litre of o·1N.AgNO$_3$ is equivalent to 11·9 grams of KBr. Therefore 816 c.c. of o·1N.AgNO$_3$ are equivalent to 11·9 × 0·816, or *9·71 grams, of KBr.*

Thus,

1 litre of the solution contains $\begin{cases} 5\cdot26 \text{ grams of } KOH, \\ 9\cdot71 \text{ grams of } KBr. \end{cases}$

116. To Determine a Solution containing NaClO and NaOH. The hypochlorite is estimated, in the presence of dilute HCl (or acetic acid), by treating aliquot portions of the solution with excess of KI and titrating the liberated iodine with standard sodium thiosulphate as described in § 67. The alkali is then determined by titration with standard HCl.

For example, 25 c.c. of a solution containing a mixture of NaClO and NaOH were acidified with dilute HCl and treated with excess of KI. As a mean of three titrations it was found that 20·0 c.c. of o·1N.Na$_2$S$_2$O$_3$ were required to reduce the iodine liberated in the reaction. It was also found that 25 c.c. of the solution required a mean volume of 27·5 c.c. of o·1N.HCl to neutralize the NaOH.

(a) *Calculation of the NaClO.* 1 litre of the solution is equivalent to 40 × 20·0, or 800 c.c., of o·1N. iodine.

Then, since 1 litre of o·1N. iodine is equivalent to 3·725 grams of NaClO (see § 67), 800 c.c. of o·1N. iodine will be equivalent to 3·725 × 0·8, or *2·98 grams, of NaClO.*

(b) *Calculation of the NaOH.* 1 litre of the solution is equivalent to 40 × 27·5, or 1100 c.c., of o·1N.NaOH.

And, since 1 litre of o·1N.NaOH contains 4·0 grams of NaOH, therefore 1100 c.c. of o·1N.NaOH are equivalent to 4·0 × 1·1, or *4·40 grams, of NaOH.*

Thus,

1 litre of the solution contains $\begin{cases} 2\cdot98 \text{ grams of } NaClO, \\ 4\cdot40 \text{ grams of } NaOH. \end{cases}$

117. The Determination of a Solution containing an Ammonium Salt and Free Ammonia. If the ammonium salt is derived from one of the halogen acids it can be estimated by titration of the neutral solution with standard silver nitrate, after the free ammonia has been determined by titration with standard acid, using *methyl red* as the indicator. If, however, the ammonium salt is not the salt of a halogen acid, the total ammonia must be estimated as described in § 28 (Method 2) : the amount of ammonium salt determined by difference.

(a) *To Determine a Solution containing NH$_4$Cl and Free NH$_3$.* (i) Aliquot portions of the solution are titrated with standard H$_2$SO$_4$ using methyl red as the indicator (methyl orange may be employed instead of methyl red, though, in

that case, the 'end-point' of the titration will not be so sharply indicated). Let the mean volume of standard acid required be n_1 c.c.

(ii) Aliquot portions of the solution are then neutralized by the addition of n_1 c.c. of standard acid (without the indicator) and titrated with standard silver nitrate solution (see § 87). The amount of NH_4Cl in the solution is then calculated from the mean titration value, n_2 c.c.

For example, in an experiment, 25 c.c. of a solution containing NH_4Cl and free NH_3 required a mean volume of 17·5 c.c. of o·1N.H_2SO_4 to neutralize the free NH_3, and 24·5 c.c. of o·1N.$AgNO_3$ to precipitate the NH_4Cl as $AgCl$.

Thus, 1 litre of the solution is equivalent to 700 c.c. of o·1N.H_2SO_4, and 980 c.c. of o·1N.$AgNO_4$.

(*i*) *Calculation of the Free* NH_3. 1 litre of o·1N.H_2SO_4 is equivalent to 1·7 grams of NH_3. Therefore, 700 c.c. of o·1N.H_2SO_4 are equivalent to 1·7 × 0·7, or *1·19 grams*, of NH_3.

(*ii*) *Calculation of the* NH_4Cl. 1 litre of o·1N.$AgNO_3$ is equivalent to 5·35 grams of NH_4Cl. Therefore, 980 c.c. of o·1N.$AgNO_3$ are equivalent to 5·35 × 0·98, or *5·24 grams*, of NH_4Cl.

Thus,

1 litre of the solution contains $\begin{cases} \textit{1·19 grams of free } NH_3, \\ \textit{5·24 grams of } NH_4Cl. \end{cases}$

(*b*) *To Determine a Solution containing* $(NH_4)_2SO_4$ *and Free* NH_3. (i) The free NH_3 is determined, as in the previous experiment, by titration with standard acid, using methyl red as the indicator. Suppose that the mean volume of standard acid required is n_1 c.c.

(ii) The *total* ammonia is then determined as described in § 28, (Method 2), and the amount of ammonium sulphate is determined by difference. Let the volume of standard acid neutralized by the total ammonia be n_2 c.c. Then, the ammonia in the ammonium sulphate is equivalent to $(n_2 - n_1)$ c.c. of standard acid.

For example, 25 c.c. of a solution containing free NH_3 and $(NH_4)_2SO_4$ required 20·0 c.c. of o·1N.H_2SO_4 to neutralize the free NH_3; i.e. 1 litre of the solution is equivalent to 800 c.c. of o·1N.H_2SO_4.

Now, 1 litre of o·1N.H_2SO_4 is equivalent to 1·7 grams of NH_3. Therefore, 800 c.c. of o·1N.H_2SO_4 are equivalent to 1·7 × 0·8, or *1·36 grams*, of NH_3.

25 c.c. of the solution were then boiled with excess of NaOH and the evolved NH_3 was absorbed in 100 c.c. of $0\cdot1$N.H_2SO_4 (see § 28, Method 2). It was found that 45 c.c. of $0\cdot1$N.NaOH were required to neutralize the excess H_2SO_4.

Therefore, (100 − 45), or 55 c.c., of $0\cdot1$N.H_2SO_4 have been neutralized by the evolved NH_3; and 20 c.c. of this are equivalent to the free NH_3 in the solution (see above).

Therefore (55 − 20), or 35 c.c., of $0\cdot1$N.H_2SO_4 are equivalent to the $(NH_4)_2SO_4$ in 25 c.c. of the solution; i.e. the $(NH_4)_2SO_4$ in 1 litre of the solution is equivalent to 35 × 40, or 1400 c.c., of $0\cdot1$N.H_2SO_4.

Now, 1 litre of $0\cdot1$N.H_2SO_4 is equivalent to 6·6 grams of $(NH_4)_2SO_4$. Therefore, 1·4 litres of $0\cdot1$N.H_2SO_4 are equivalent to 6·6 × 1·4, or *9·24 grams, of $(NH_4)_2SO_4$.*

Thus,

1 litre of the solution contains $\begin{cases} \textit{1·36 grams of free } NH_3, \\ \textit{9·24 grams of } (NH_4)_2SO_4. \end{cases}$

118. The Determination of a Solution containing an Ammonium Salt and Caustic Alkali. If the ammonium salt is the derivative of a halogen acid the mixture is best estimated by determining the alkali with standard acid (methyl orange is the best indicator to use in this case), and then determining the ammonium halide by titration, in neutral solution, with standard silver nitrate (see § 87).

If, however, the ammonium salt is not a halide, then it is best estimated by the method, 1, described in § 28. The actual procedure depends upon whether the amount of caustic alkali is in excess or not; e.g. :

To Determine a Solution containing $(NH_4)_2SO_4$ and NaOH.
(a) *When the NaOH is Present in Excess.* (i) The NaOH is determined by titration with standard acid, using methyl orange as the indicator (as an ammonium salt is present).

(ii) The ammonium salt is then determined by boiling a portion of the solution. The residual NaOH is then determined by titration with standard acid, using methyl orange as the indicator. The amount of NaOH equivalent to the ammonium salt is then found by difference.

(b) *When the NaOH is Not Present in Excess.* (i) The NaOH is determined as before. Suppose that n_1 c.c. of decinormal acid were required to neutralize the NaOH in a given volume of the solution.

(ii) A measured excess of $0\cdot1$N.NaOH (n_2 c.c.) is then added to the same amount of solution as was taken in (i),

and the ammonia in the ammonium salt is determined as in § 28 (Method 1).   Suppose that n_3 c.c. of decinormal acid were required to neutralize the excess NaOH.

Then, the NH_3 in the ammonium salt is equivalent to $(n_1 + n_2 - n_3)$ c.c. of decinormal acid.

For example, in an experiment, it was found that 25 c.c. of a solution containing ammonium sulphate and NaOH required a mean volume of 21·0 c.c. of 0·1N.H_2SO_4 to neutralize the NaOH.

25 c.c. of 0·1N.NaOH were then added to 25 c.c. of the solution, and the mixture was boiled until the evolution of ammonia ceased.   On cooling, it was found that 17·6 c.c. of 0·1N.H_2SO_4 were required to neutralize the excess NaOH.

(i) *Calculation of the NaOH.*   1 litre of the solution contains 40 × 21, or 840 c.c., of 0·1N.NaOH ; i.e. 4·0 × 0·84, or *3·36 grams, of NaOH.*

(ii) *Calculation of the $(NH_4)_2SO_4$.*   The ammonium sulphate in 1 litre of solution is equivalent to 40 × (21 + 25 − 17·6), or 1136 c.c., of 0·1N.H_2SO_4.   And 1 litre of 0·1N.H_2SO_4 is equivalent to 6·6 grams of $(NH_4)_2SO_4$.

Therefore, 1·136 litres of 0·1N.H_2SO_4 are equivalent to 6·6 × 1·136, or *7·30 grams, of $(NH_4)_2SO_4$.*

Thus,

1 litre of the solution contains $\begin{cases} \textit{3·36 grams of NaOH,} \\ \textit{7·30 grams of } (NH_4)_2SO_4. \end{cases}$

119.   To Determine a Mixture of an Ammonium Halide and another Ammonium Salt.   (a) An accurately known weight of the mixture is dissolved in distilled water, neutralized if necessary, and diluted to a convenient volume.   Aliquot portions are then titrated with standard silver nitrate, and the ammonium halide is determined from the mean titration value.

(b) The total ammonia is then determined by either of the methods described in § 28.   The amount of the second ammonium salt is then estimated by difference.

For example, 25 c.c. of a solution containing NH_4Cl and NH_4NO_3 required a mean volume of 20·0 c.c. of 0·1N.$AgNO_3$ to precipitate the NH_4Cl.

Another 25 c.c. of the solution were mixed with 100 c.c. of 0·1N.NaOH, boiled until the evolution of NH_3 ceased, cooled, and titrated with 0·1N.H_2SO_4, 32·5 c.c. of which were required.

(a) *Calculation of the NH_4Cl.*   1 litre of 0·1N.$AgNO_3$ is

equivalent to 5·35 grams of NH_4Cl. Therefore, 20 c.c. of 0·1N.$AgNO_3$ are equivalent to 5·35 × 0·02, or *0·107 gram*, of NH_4Cl.

(b) *Calculation of the NH_4NO_3.* The *total* ammonia is equivalent to (100 − 32·5), or 67·5 c.c., of 0·1N.H_2SO_4. Therefore, the NH_3 in the NH_4NO_3 is equivalent to (67·5 − 20·0), or 47·5 c.c., of 0·1N.H_2SO_4.

Then, since 1 litre of 0·1N.H_2SO_4 is equivalent to 8·0 grams of NH_4NO_3, 47·5 c.c. of 0·1N.H_2SO_4 are equivalent to 8·0 × 0·0475, or *0·380 gram, of NH_4NO_3.*

Thus, the percentage of NH_4Cl in the mixture is

$$\frac{0·107}{0·487} \times 100, \text{ or } 21·9\% ;$$

and the percentage of NH_4NO_3 is

$$\frac{0·380}{0·487} \times 100, \text{ or } 78·1\%.$$

120. To Determine a Solution containing an Alkaline Carbonate and an Inorganic Halide. (i) Aliquot portions of the solution are titrated with standard H_2SO_4, using methyl orange as the indicator, and the amount of carbonate in the solution is determined from the mean titration value. Let this titration value be n c.c.

(ii) Aliquot portions of the solution are then neutralized by the addition of n c.c. of standard H_2SO_4 (without the indicator)*, and the halide is determined by titration with standard $AgNO_3$ (see § 87).

For example, 25 c.c. of a solution containing sodium carbonate and sodium chloride required a mean volume of 21·6 c.c. of 0·1N.H_2SO_4 to neutralize the sodium carbonate, and an additional 20·8 c.c. of 0·1N.$AgNO_3$ to precipitate all the chloride as silver chloride.

Then, 1 litre of the solution is equivalent to 864 c.c. of 0·1N.H_2SO_4, and to 832 c.c. of 0·1N.$AgNO_3$.

(a) *Calculation of the Na_2CO_3.* 1 litre of 0·1N.H_2SO_4 is equivalent to 5·3 grams of Na_2CO_3. Therefore, 864 c.c. of 0·1N.H_2SO_4 are equivalent to 5·3 × 0·864, or *4·58 grams, of Na_2CO_3.*

(b) *Calculation of the NaCl.* 1 litre of 0·1N.$AgNO_3$ is equivalent to 5·85 grams of NaCl. Therefore 832 c.c. of 0·1N.$AgNO_3$ are equivalent to 5·85 × 0·832, or *4·87 grams, of NaCl.*

* Boil to expel CO_2 and allow to cool.

Thus,

1 litre of the solution contains $\begin{cases} 4 \cdot 58 \text{ grams of } Na_2CO_3, \\ 4 \cdot 87 \text{ grams of } NaCl. \end{cases}$

121. To Determine a Solution containing an Alkaline Cyanide and a Ferrocyanide. (a) Aliquot portions of the solution are titrated with standard silver nitrate, and the cyanide is determined from the mean titration value (see § 91).

(b) A standard solution of zinc is prepared by dissolving 1 gram of pure zinc-foil in pure, dilute H_2SO_4 (a large excess of acid must be avoided), and the solution is diluted to 250 c.c. Aliquot portions of the solution are then titrated with the solution containing the ferrocyanide, at a temperature not below 90° C., using uranyl acetate as an external indicator; the titration must be carried out slowly (see § 106). The ferrocyanide is then determined from the mean titration value, employing the equivalents (in the case of potassium ferrocyanide) :

$$2K_4Fe(CN)_6 \equiv 3Zn.$$
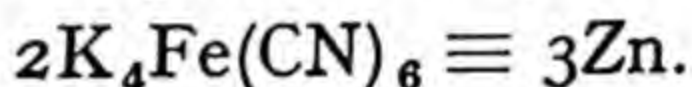
For example, 25 c.c. of a solution containing a mixture of potassium cyanide and potassium ferrocyanide required a mean titration of 18·5 c.c. of 0·1N.$AgNO_3$ to convert the KCN to the double cyanide, $KAg(CN)_2$ (for method see § 91); i.e. 1 litre of solution $\equiv$ 740 c.c. 0·1N.$AgNO_3$.

A further 25 c.c. of the solution required a mean volume of 52·0 c.c. of a standard zinc solution (1 c.c. $\equiv$ 0·004 gram of Zn) to effect the brown coloration with uranyl acetate; i.e. 1 litre $\equiv$ 2·08 litres of Zn solution.

(a) Calculation of the KCN. 1 litre of 0·1N.$AgNO_3$ is equivalent to 13·0 grams of KCN (see § 91). Therefore, 740 c.c. of 0·1N.$AgNO_3$ are equivalent to 13·0 × 0·74, or 9·62 grams, of KCN.

(b) Calculation of the Ferrocyanide. 2·08 litres of Zn solution contain 2·08 × 4, or 8·32 grams, of Zn.

Thus, 1 litre of the mixture is equivalent to 8·32 grams of Zn.

Now, $3Zn \equiv 2K_4Fe(CN)_6$;

i.e. 3 × 65·4 grams of Zn $\equiv$ 2 × 368 grams of $K_4Fe(CN)_6$.

Thus, 8·32 grams of Zn $\equiv$

$\dfrac{2 \times 368}{3 \times 65 \cdot 4} \times 8\cdot32$, or 31·22 grams, of $K_4Fe(CN)_6$.

Thus,

1 litre of the solution contains $\begin{cases} 9 \cdot 62 \text{ grams of } KCN, \\ 31 \cdot 22 \text{ grams of } K_4Fe(CN)_6. \end{cases}$

SUGGESTED EXPERIMENTS ON CHAPTER VIII

1. You are given an aqueous solution, A, containing a known weight of KCl, and a solution, B, containing a known weight of hydrated potassium oxalate. You are provided with decinormal solutions of silver nitrate and potassium permanganate, and are asked to find (a) the equivalent of the metal, (b) the percentage of water of crystallization in the hydrated oxalate.

2. You are provided with decinormal solutions of silver nitrate and sodium hydroxide, and are required to determine the respective amounts of calcium chloride and HCl in 1 litre of the given solution.

3. You are provided with a normal solution of KOH and a decinormal solution of potassium permanganate, and are asked to determine the respective amounts of ferrous sulphate and sulphuric acid in 1 litre of the given solution.

4. You are provided with decinormal sulphuric acid and solid silver nitrate. Determine the respective amounts of NaOH and NaCl in 1 c.c. of the given solution.

5. You are given a mixture containing sodium carbonate, sodium bicarbonate and sodium chloride. You are provided with decinormal solutions of NaOH and silver nitrate, and are asked to determine the percentage composition of the mixture.

6. You are provided with a solution containing a small amount of ammonium sulphate and a comparatively large amount of NaOH. Given a normal solution of sulphuric acid determine the amount of each constituent in 1 litre of the given solution.

7. You are asked to determine the percentage composition of the given mixture of ammonium chloride and ammonium nitrate. You are provided with decinormal silver nitrate and normal NaOH.

8. You are provided with decinormal solutions of iodine and HCl, and are required to determine the respective amounts of sodium thiosulphate and NaOH in 1 litre of the given solution.

9. You are provided with a mixture of potassium nitrate and nitrite. Devise, and employ, a method for estimating the composition of the mixture.

10. You are provided with a solution of stannous chloride in dilute HCl. Devise, and employ, two alternative methods for the determination of each constituent in 1 litre of the solution. Compare the two results, and, if there is any discrepancy, suggest a reason for the difference.

11. You are provided with stick KOH, normal sulphuric acid, and decinormal potassium permanganate, and are asked to determine the respective amounts of oxalic acid and potassium hydrogen oxalate in 1 litre of the given solution.

12. Devise, and employ, a method for estimating the respective amounts of KCN and potassium ferrocyanide, in 1 litre of the given solution.

13. Devise, and employ, a method for the determination of a solution containing NaH_2PO_4 and Na_2HPO_4.

14. Given pure ferrous ammonium sulphate and decinormal NaOH, determine a solution of HCl containing potassium dichromate.

CHAPTER IX

AN IMPORTANT APPLICATION OF VOLUMETRIC ANALYSIS : SOLUBILITIES

122.   If a compound can be estimated, in solution, by any volumetric method, then it is generally possible to determine its solubility in the same solvent by the same method, or by some modification of that method.

In general, a saturated solution of the substance is prepared, at the particular temperature desired ; the solution is diluted to a convenient volume and titrated with the specific standard solution.   This method applies particularly to solids, but, in several cases, it is also applicable to dissolved liquids and gases (especially where the gas has a high solubility).

THE SOLUBILITIES OF SOLIDS

The solubility of a solid is usually expressed as a percentage ; i.e. the number of grams of the solid which will dissolve in 100 grams of a solvent at a particular temperature.

The solubility of a solid is generally determined volumetrically by making a saturated solution of the solid, in the given solvent, at the temperature desired, and then diluting the solution considerably.   Aliquot portions of the diluted solution are then titrated with the specific standard reagent, and the solubility is calculated from the titration values.   In the case of an aqueous solution of a solid, if the degree of dilution of the saturated solution has been considerable it is customary to express the solubility of the solid as the amount of solid dissolved in 100 c.c. of solution, and to assume that this value approximates very nearly to the true solubility.   This assumption is quite justifiable where the dilution of the saturated solution has been very great, but very little extra trouble is experienced by taking a weighed quantity of the saturated solution, diluting, titrating with the required standard reagent, and then expressing the solubility directly as a percentage.   With any other solvent than water this method must be employed.

For example, suppose that w_1 grams of the saturated solution are taken, and that it is found from the subsequent

titration of this amount of solution that w_2 grams of the solid are present in the w_1 grams of solution.

Then, the solubility of the solid will be given by the expression :

$$\frac{100 w_2}{w_1 - w_2}.$$

N.B.—Where the solubility has to be determined at temperatures above that of the room, a saturated solution is made in a vessel, immersed in a thermostat at a temperature a few degrees above the required temperature ; the solution is then allowed to cool slowly, and, directly the required temperature is reached, a suitable quantity of the solution is withdrawn into a weighed vessel and its weight determined. The solubility is then determined in the ordinary way.

123. THE DETERMINATION OF THE SOLUBILITY OF SODIUM CHLORIDE AT ROOM TEMPERATURE. A saturated solution of pure NaCl was prepared at room temperature, and a portion of the solution was transferred to a clean, dry, weighed flask. The weight of the solution was then determined and was found to be 33·89 grams. The portion of the saturated solution was then diluted to 1 litre with distilled water, and aliquot portions were titrated with 0·1N.AgNO$_3$. It was found that a mean volume of 38·0 c.c. of the 0·1N.AgNO$_3$ was needed to precipitate all the chlorine, in 25 c.c. of solution, as silver chloride.

Thus, 1 litre of the diluted NaCl solution is equivalent to 38 × 40, or 1520 c.c., of 0·1N.AgNO$_3$.

Then, since 1 litre of 0·1N.AgNO$_3$ is equivalent to 5·85 grams of NaCl, 1·52 litres of 0·1N.AgNO$_3$ are equivalent to 5·85 × 1·52, or 8·89 grams, of NaCl.

Therefore, 33·89 grams of saturated NaCl solution contain, at room temperature, 8·89 grams of NaCl.

Thus, the solubility of NaCl, at room temperature, is

$$\frac{100 \times 8\cdot89}{33\cdot89 - 8\cdot89} \text{ or } 35\cdot56\%.$$

124. THE SOLUBILITIES OF AMMONIUM SALTS. The solubility of an ammonium salt may be determined by preparing a saturated solution of the salt, at the required temperature, and diluting a known weight (w_1) of the solution. The ammonia in the portion of saturated solution is then determined by either of the methods described in § 28, and the amount of ammonium salt in the solution is then calculated.

Let this amount be w_2 grams. Then, the solubility of the ammonium salt is given by the expression

$$\frac{100w_2}{w_1 - w_2}.$$

N.B.—In the case of ammonium chloride, or the ammonium salt of any other halogen acid, the silver nitrate method (as employed in § 87) is much more convenient.

125. THE SOLUBILITY OF OXALIC ACID. A saturated solution of the acid is prepared at the particular temperature desired ; a weighed amount (w_1) of the solution is diluted to suitable volume, and titrated with standard NaOH or $KMnO_4$. Then, if w_2 grams of oxalic acid are present in w_1 grams of solution, the solubility of the acid is given by the expression

$$\frac{100w_2}{w_1 - w_2}.$$

126. THE SOLUBILITIES OF FERROUS AND FERRIC SALTS. (a) *Ferrous Salts.* Make a saturated solution of the ferrous salt at the required temperature, and dilute a known weight (w_1) of the solution to a convenient volume. Titrate aliquot portions of the solution with standard $KMnO_4$ (see § 36 ; in the case of ferrous chloride standard $K_2Cr_2O_7$ must be used in preference to $KMnO_4$, see § 52). The amount of ferrous salt (w_2) in the known weight of saturated solution is then determined from the mean titration value. The solubility is then given by the expression

$$\frac{100w_2}{w_1 - w_2}.$$

(b) *Ferric Salts.* A saturated solution of the salt is prepared at the required temperature. A weighed amount (w_1) of the solution is then diluted, and aliquot portions are reduced to the ferrous state by one or other of the methods given in § 37. The amount (w_2) of ferric salt is then determined by titration with standard $KMnO_4$ (or standard $K_2Cr_2O_7$ in the case of ferric chloride ; the zinc acid method of reduction must not be employed in this determination). The solubility is then determined from the expression

$$\frac{100w_2}{w_1 - w_2}.$$

127. THE SOLUBILITY OF POTASSIUM DICHROMATE. Make a saturated solution of the compound at the required temperature, and dilute a weighed amount (w_1) to a suitable volume. Titrate aliquot portions of the solution with a standard solution of ferrous ammonium sulphate (see § 50), and calculate

the amount of the dichromate (w_2) in w_1 grams of solution. Deduce the solubility from the expression

$$\frac{100 w_2}{w_1 - w_2}.$$

128. THE SOLUBILITY OF SOLUBLE SILVER SALTS. Prepare a saturated solution of the silver salt at the required temperature. Dilute w_1 grams of the saturated solution to a convenient volume, and titrate aliquot portions with standard NaCl solution (see § 96). Calculate the amount of silver salt (w_2) in w_1 grams of the saturated solution. The solubility is determined from the expression

$$\frac{100 w_2}{w_1 - w_2}.$$

129. THE SOLUBILITY OF SODIUM THIOSULPHATE. Make a saturated solution of sodium thiosulphate at the required temperature, and dilute w_1 grams of the solution to a suitable volume. Titrate aliquot portions of the diluted solution with standard iodine solution (see § 59 (a)). Calculate the amount of $Na_2S_2O_3.5H_2O$ (w_2) in w_1 grams of the solution. The solubility is then determined from the expression

$$\frac{100 w_2}{w_1 - w_2}.$$

130. THE SOLUBILITY OF ANTIMONYL POTASSIUM TARTRATE. Make a saturated solution of the tartrate at the desired temperature. Dilute w_1 grams of the saturated solution to a convenient volume, and titrate aliquot portions of this solution with standard iodine solution (see § 61 (a)), and estimate the amount of tartrate (w_2) in w_1 grams of the saturated solution from the equivalents :

$$I_2 \equiv (SbO)KC_4H_4O_6.\tfrac{1}{2}H_2O.$$
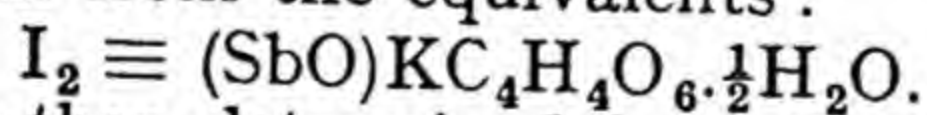
The solubility is then determined from the expression

$$\frac{100 w_2}{w_1 - w_2}.$$

131. THE SOLUBILITY OF POTASSIUM IODATE. Prepare a saturated solution of the iodate at the desired temperature, and dilute w_1 grams of the solution to a convenient volume. Estimate the amount of iodate (w_2) in w_1 grams of saturated solution by treating aliquot portions of the diluted solution with excess of KI and titrating the liberated iodine with standard sodium thiosulphate, as described in § 69. The solubility is determined from the expression

$$\frac{100 w_2}{w_1 - w_2}.$$

132. THE SOLUBILITY OF POTASSIUM BROMATE. Make a saturated solution of the bromate at the required temperature and dilute w_1 grams of the solution to a suitable volume, Estimate the weight of bromate (w_2) by means of KI and standard sodium thiosulphate, as described in § 70. Calculate the solubility of the bromate from the expression

$$\frac{100w_2}{w_1 - w_2}.$$

133. THE SOLUBILITY OF POTASSIUM CHROMATE. Make a saturated solution of the chromate at the required temperature, and dilute w_1 grams of the solution to a suitable volume. Estimate the amount of chromate (w_2) in w_1 grams of saturated solution by means of KI and standard sodium thiosulphate, as described in § 71. Calculate the solubility from the expression

$$\frac{100w_2}{w_1 - w_2}.$$

134. THE SOLUBILITIES OF LIQUIDS. Volumetric methods may be employed, in suitable cases, for the determination of solubilities of liquids in water. The methods may be employed, if practicable, not only to liquids which are miscible in all proportions with water, but also to those liquids which are only partially miscible with water: e.g.:

To Determine the Solubility of Aniline in Water at Room Temperature. The solubility of aniline in water is generally determined by means of a standard solution of a mixture of potassium bromide and potassium bromate. As in the case of the standard solution of a mixture of potassium iodate and potassium iodide (see § 84), the constituents must be in the molecular proportions $5KBr : KBrO_3$. This solution is best prepared by carefully adding bromine to a saturated solution of KOH until no more bromine is dissolved; the solution is then diluted in order to dissolve any bromate which may have crystallized out, and a little more bromine is added. Bromine water is then added cautiously until the solution has a faint alkaline reaction only.

Standardization of the Bromide-bromate Solution (see § 108). The solution is standardized by means of a standard aniline solution. 0·5 gram of aniline is weighed accurately and dissolved in 20 c.c. of water, to which 10 c.c. of concentrated HCl have been added. The aniline is thus brought into solution in the form of aniline hydrochloride.

▸ Thus, 1 c.c. of the aniline solution is equivalent to 0·025 gram of aniline.

10 c.c. of this solution (0·25 gram of aniline) are then titrated with the bromide-bromate solution, the solution being well shaken after each addition. A white precipitate of tri-bromaniline is obtained and the supernatant liquid is, at first, colourless, but directly there is the slightest excess of evolved bromine it turns a faint yellow; this marks the 'end-point' of the titration. The remaining 10 c.c. of the standard aniline solution are then titrated with the bromide-bromate solution, and the solution is then standardized from the mean titration value.

The reactions which take place are as follow:

(i) The HCl liberates the free acids, in solution, from the bromide and the bromate:

$$5KBr + KBrO_3 + 6HCl = HBrO_3 + 5HBr + 6KCl.$$

(ii) These two acids then interact with the liberation of bromine:

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$
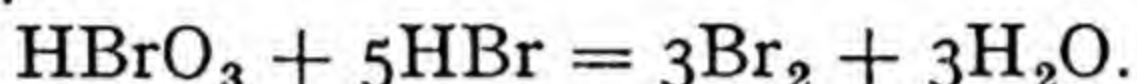
(iii) The bromine attacks the aniline with the formation of tribromaniline, the 'end-point' of the reaction being indicated by the appearance of the faint yellow colour of the first trace of excess bromine:

$$C_6H_5NH_2 + 3Br_2 = C_6H_2Br_3NH_2 + 3HBr.$$
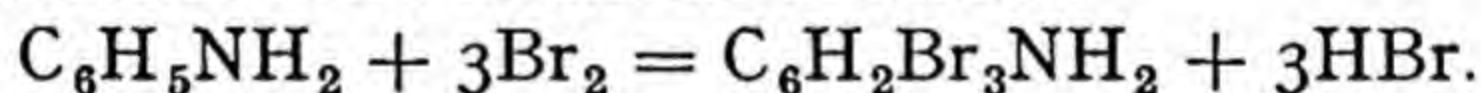
The Determination. About 20 c.c. of aniline are thoroughly shaken with 100 c.c. of water, and the solution is then allowed to settle. It will be seen that there are two distinct layers: an upper layer consisting of an aqueous solution of aniline, and a lower layer of a solution of water in aniline. 10 c.c. of the upper layer are withdrawn and titrated with the standard bromide-bromate solution as described above. Three concordant results are obtained, and the solubility of the aniline in water obtained from the mean titration value.

135. THE VOLUMETRIC DETERMINATION OF THE SOLUBILI-TIES OF EXTREMELY SOLUBLE GASES. With the exception of chlorine, the solubilities of gases which are only sparingly soluble in water cannot be determined accurately by volumetric methods; but extremely soluble gases, such as hydrogen chloride, ammonia, and sulphur dioxide, are best determined by volumetric methods. The reason for this is that an extremely soluble gas does not obey Henry's Law, except at fairly high temperatures, and its solubility, at low temperatures, cannot therefore be determined by the direct application of Henry's Law.

The solubility of a gas is defined as *the number of c.c. of the*

gas dissolved by 1 c.c. of the solvent. This volume reduced to normal temperature and pressure is known as the *Coefficient of Absorption* of the gas.

136. TO DETERMINE THE SOLUBILITY OF AMMONIA IN WATER AT 0° C.

The apparatus consists of a U-tube of thin glass with a bulb blown at the bend. It is weighed empty (w_1), and air-free distilled water is then introduced until the bulb is about three-quarters filled. The tube is then placed in a large beaker containing a mixture of ice and water (the determination is thus carried out at 0° C.). The tube is then attached at C to an apparatus for the preparation of pure, *dry* ammonia, and a steady stream of ammonia gas is passed through the tube until no more ammonia is absorbed by the water in the bulb. The generator is then detached and the U-tube sealed at B, and then at A by means of a mouth blowpipe. The
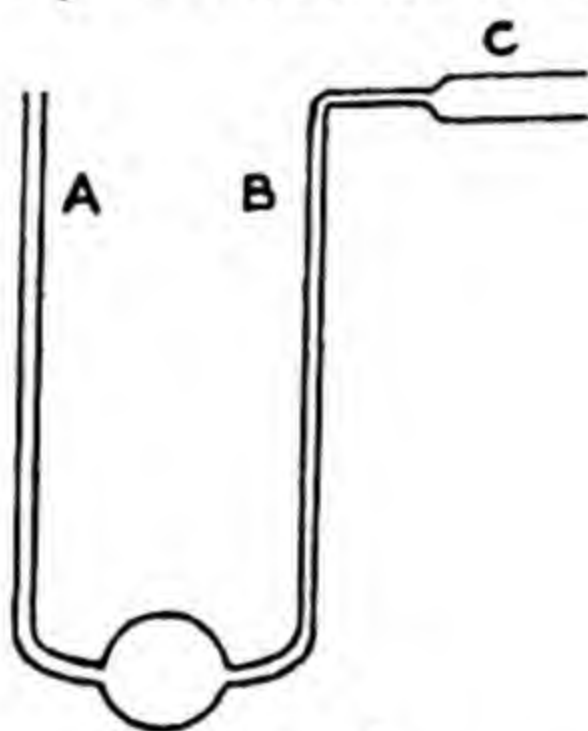
FIG. 6

APPARATUS FOR DETERMINATION OF THE SOLUBILITY OF A GAS

tube is then re-weighed, together with the piece of glass removed from B in sealing the tube. Suppose that this weight is w_2 grams :

Then the weight of the saturated solution of the gas is $w_2 - w_1$ grams.

The U-tube is then immersed in a measured excess of $N.H_2SO_4$, and the bulb is broken by means of a piece of glass tubing ; the ammonia thus combines with the sulphuric acid forming ammonium sulphate. The excess $N.H_2SO_4$ is then determined by titration with N.NaOH, using methyl orange as the indicator ; the weight of ammonia (w_3) in the saturated solution is then calculated from the titration value.

Thus, the weight of water will be $(w_2 - w_1) - w_3$ grams.

Therefore 1 gram of water will dissolve $\dfrac{w_3}{(w_2 - w_1) - w_3}$ grams of ammonia.

The coefficient of absorption of ammonia in water can then be calculated from the data ; 1 litre of hydrogen, at N.T.P., weighs 0·09 gram, and the vapour density of ammonia is 8·5.

Thus, 1 litre of ammonia, at N.T.P., weighs 0·09 × 8·5, or 0·765 gram.

For example, in an experiment, the following results were obtained :

Weight of saturated solution of NH_3 = 7·576 grams.

Temperature of solution = 0° C.

Volume of $N.H_2SO_4$ = 250 c.c.

Volume of N.NaOH required to neutralize the excess H_2SO_4 = 52·5 c.c.

Thus, (250 − 52·5), or 197·5 c.c., of $N.H_2SO_4$ have been required to neutralize the saturated solution of NH_3 ; i.e. 7·576 grams of saturated NH_3 solution contain the equivalent of 197·5 c.c. of $N.NH_3$.

Therefore, 197·5 × ·017, or 3·3575 grams, of NH_3 are contained in 7·576 grams of the saturated solution.

Thus, (7·576 − 3·3575), or 4·2187 grams, of water have dissolved 3·3575 grams of NH_3 at 0° C.

Therefore, 1 gram of water dissolves $\frac{3·3575}{4·2187}$, or *0·7959 gram, of NH₃ at 0° C.*

Calculation of the Coefficient of Absorption of NH₃. 1 litre of NH_3 weighs 0·765 gram (see above). Therefore, 0·7959 gram of NH_3 at N.T.P. will occupy a volume of $\frac{0·7959}{0·7650}$ × 1000, or *1050 c.c.*

Thus, 1 c.c. of water, at 0° C., will dissolve 1050 c.c. of ammonia measured at 0° C. and 760 mm. of mercury.

N.B.—If the solubility of the gas has to be determined at a temperature above 0° C., a thermostat must be employed.

137. THE SOLUBILITY OF HCl IN WATER. Perfectly dry HCl is used, and the saturated solution of the gas is obtained in the same way as for ammonia (see § 136). The bulb is broken under excess of a N.NaOH solution, and the excess NaOH is determined by titration with standard acid, using litmus as the indicator. The solubility of the HCl is then determined from the weighings and the titration value, in exactly the same way as for ammonia (§ 136).

138. THE SOLUBILITY OF SULPHUR DIOXIDE IN WATER. Gaseous sulphur dioxide from a siphon is employed, and a saturated solution of the gas at 0° C. is prepared in exactly the same way as in the case of ammonia (see § 136). The

bulb containing the saturated solution of SO_2 is broken under excess of standard $KMnO_4$, and the excess $KMnO_4$ is determined by titration with standard oxalic acid solution. It is preferable to work with *one-fifth normal* solutions. The weight of SO_2 in the saturated solution is determined from the mean titration value, and the solubility is then determined exactly as in the case of ammonia (see § 136).

An alternative method is to break the bulb containing the saturated solution of SO_2 under a standard iodine solution; it is advisable, however, to add a large excess of distilled water to the iodine solution as SO_2 is only estimated accurately, iodometrically, when in dilute solution. The excess iodine is estimated by titration with standard sodium thiosulphate solution, and the solubility determined as before.

139. THE SOLUBILITY OF CHLORINE. Although chlorine is a gas which is not extremely soluble in water, its solubility may be determined volumetrically by preparing a saturated solution of the pure, dry gas in water, as in the case of ammonia (see § 136). The bulb containing the saturated solution is broken under a solution of KI and the liberated iodine determined by titration with standard sodium thiosulphate. The solubility is then determined exactly as in the case of ammonia (see § 136).

SUGGESTED EXPERIMENTS ON CHAPTER IX

1. You are provided with decinormal silver nitrate solution, and are required to determine the solubility of KCl, KBr, and KI respectively at the temperature of the laboratory.

2. You are provided with decinormal potassium permanganate and are asked to determine the solubilities of (a) hydrated potassium oxalate at 60° C., (b) ferrous ammonium sulphate at 25° C., and (c) iron alum at laboratory temperature.

3. Given pure ferrous ammonium sulphate determine the solubility of potassium dichromate at the laboratory temperature.

4. Given a decinormal solution of iodine determine the solubilities of (a) hydrated sodium thiosulphate, (b) sodium arsenite, both at the temperature of the laboratory.

5. You are provided with potassium iodide and decinormal sodium thiosulphate, and are required to determine the solubilities of (a) potassium iodate, (b) potassium bromate, and (c) potassium chromate at the temperature of the laboratory.

6. You are provided with normal solutions of HCl and NaOH, and are asked to determine the solubilities, at 0° C., of (a) ammonia gas, and (b) hydrogen chloride.

7. Devise, and employ, an alternative volumetric method to that described in § 138 for the determination of the solubility of sulphur dioxide. Carry out the determination at the temperature of the laboratory.

CHAPTER X

THE THEORY OF INDICATORS

140. The modern theory of indicators is based upon the ionic theory and upon the law of mass action. As indicators are generally employed in aqueous solution, it is best, therefore, to commence with a study of water from the standpoints of the ionic theory and the law of mass action.

According to the ionic theory, water is regarded as being slightly dissociated into electropositive hydrogen ions and electronegative hydroxyl ions :

$$H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{OH}.$$
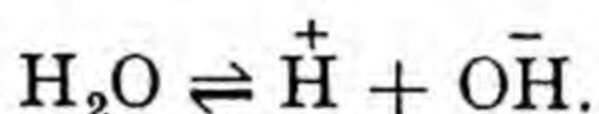
Suppose that C_{H_2O}, C_H, and C_{OH} are the concentrations, in *gram-equivalents per litre*, of the undissociated water, the hydrogen ions, and the hydroxyl ions respectively.

Then, by the law of mass action,

$$\frac{C_H \times C_{OH}}{C_{H_2O}} = \text{Constant}\dots\dots\dots\dots(1)$$

Now, since the amount of ionization is very small, the concentration of the unionized water must be very large in comparison with the ionic concentrations, and may, therefore, be taken as constant.

Thus equation (1) becomes

$$C_H \times C_{OH} = C_{H_2O} \times \text{Constant} = K_W\dots\dots\dots(2)$$

where K_W is a constant known as the *ionic product* of water.

This product has been determined in various ways, and all the results give the value approximately as 10^{-14} at a temperature of 24° C. Consequently, since $C = C_{OH}$, the concentration of both hydrions and hydroxyl ions in pure water, or in any neutral solution, will be 10^{-7} gram-equivalents per litre (i.e. only one molecule of water in ten million is completely ionized) at 24° C.

141. THE HYDROGEN ION CONCENTRATION OF ACID AND ALKALINE SOLUTIONS. We have just seen that, in a neutral solution, the concentration of both hydrions and hydroxyl ions is the same, viz. 10^{-7} gram-equivalents per litre at 24° C., and that the product of the ionic concentrations at the same

temperature is constant, viz. 10^{-14}. If a small quantity of acid is added to pure water, or a neutral solution, the hydrogen ion concentration will increase beyond the value 10^{-7}, and, consequently, since the ionic product is constant, the hydroxyl ion concentration will fall below 10^{-7}. Conversely, if an alkali is added to pure water, or a neutral solution, the hydroxyl ion concentration will increase beyond 10^{-7}, and, consequently, the hydrogen ion concentration will fall below 10^{-7}. Thus, any solution which has a hydrogen ion concentration greater than 10^{-7} will be acidic, and if the hydrogen ion concentration is below 10^{-7} the solution will be alkaline. *Thus, in titrating an acid, or a base, the hydrogen ion concentration of the titration mixture will be continuously changing.*

It will be apparent, at once, that it is possible to have solutions possessing different 'degrees of acidity'. For example, we may have a series of 'acid' solutions in which the hydrogen ion concentration may vary from, say, 10^{-1} to 10^{-6}. Similarly, the range of alkalinity may be equally great. In view of this it is not surprising to find that different indicators give varying results in certain titrations. The concentrations of hydrogen and hydroxyl ions in solutions have been determined by various independent methods, and it is, therefore, quite simple to prepare solutions of known ionic concentrations and to test their behaviour with regard to different indicators. The following table shows the ranges of sensitiveness for the common indicators :

Indicator	Range of C_H over which the Colour Change is Effective in Accurate Titration		
Methyl Orange..	$10^{-3.1}$	to	$10^{-4.4}$
Methyl Red	$10^{-4.4}$	to	$10^{-6.0}$
Paranitrophenol	$10^{-5.0}$	to	$10^{-7.0}$
Litmus	$10^{-5.0}$	to	$10^{-8.0}$
Phenolphthalein	$10^{-8.0}$	to	$10^{-9.0}$

142. THE MODERN THEORY OF INDICATORS. According to modern theory all indicators are regarded as weak acids or weak bases. In fact, we may say that any weak acid can be used as an indicator if it gives, in solution, a negative ion which is coloured differently from the undissociated molecule, and that any weak base can be used as an indicator if it gives,

in solution, a positive ion which is coloured differently from the undissociated molecule.

Thus an indicator which is a weak acid, and which is colourless in the unionized state and coloured when ionized, may be represented as behaving as follows :

$$\underset{\text{colourless}}{\text{HA}} \quad \rightleftharpoons \quad \underset{\text{coloured}}{\overset{+}{\text{H}} + \overset{-}{\text{A}}}$$
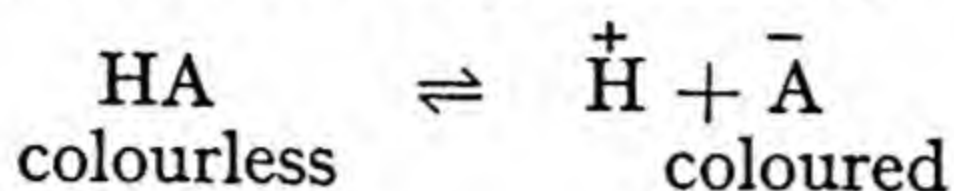
It is evident that the acid must be weak so that a slight excess of hydrogen or hydroxyl ions added to the solution will produce a colour change. For example, in the above case an excess of $\overset{+}{\text{H}}$ ions will destroy the slight dissociation of the indicator governed by the expression :

$$\frac{C_H \times C_A}{C_{HA}} = K_I \text{ (the Dissociation Constant of the indicator)},$$

and so the solution becomes colourless. If, however, a base is added to the aqueous solution of the indicator, the highly ionized salt of the indicator and the base is formed, and, as the negative ion is coloured, the solution will also be coloured. On the other hand, the acid must not be too weak, for with excess of base the salt formed by the interaction of the base and the acid indicator will be hydrolyzed considerably (see § 9), and the colour change would occur before true equivalence had been attained.

An indicator which is a weak base and which is colourless in the unionized state will dissociate, in aqueous solution, into ions :

$$\underset{\text{colourless}}{\text{XOH}} \quad \rightleftharpoons \quad \underset{\text{coloured}}{\overset{+}{\text{X}} + \overset{-}{\text{OH}}}$$
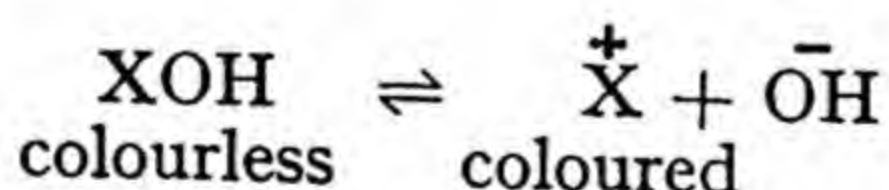
A slight excess of $\overset{-}{\text{OH}}$ ions added to the solution will destroy the slight dissociation of the indicator governed by the expression

$$\frac{C_X \times C_{OH}}{C_{XOH}} = K_I,$$

and so the solution would become colourless. On the other hand, if an acid is added to the solution the highly ionized salt of the acid and the basic indicator would be formed, and, as the positive ion is coloured, the solution would also be coloured.

EXAMPLES OF ACID INDICATORS

(a) *Paranitrophenol.* Paranitrophenol is a fairly strong acid indicator ; the un-ionized molecule is colourless and the negative ion is yellow in aqueous solution :

$$HO.C_6H_4.NO_2 \rightleftharpoons \overset{+}{H} + O.\overset{-}{C_6}H_4.NO_2.$$

colourless   yellow

When an acid is added to an aqueous solution of paranitrophenol the ionization of the indicator is suppressed, and, consequently, the solution becomes colourless. When, however, a base is added to the indicator solution the highly ionized salt of the base and paranitrophenol is formed so the solution turns yellow owing to the presence of the free negative ions. Since paranitrophenol is a moderately strong acid, it is used in the tritation of weak bases by strong acids ; the salt of the paranitrophenol which is formed in the titration will not be greatly hydrolyzed, so that the colour change is given without too great a loss of sensitiveness.

(b) *Phenolphthalein.* Phenolphthalein is the weakest acid indicator known. In aqueous solution the unionized molecule is colourless and the negative ion red, viz. :

$$HPh \rightleftharpoons \overset{+}{H} + \overset{-}{Ph}$$

colourless   red

When an acid is added to the solution of the indicator the slight dissociation is suppressed, and, consequently, the solution becomes colourless. If, however, a base is added to the solution the strongly ionized salt of the base and phenolphthalein is formed, and the solution will, therefore, be coloured red. As phenolphthalein is such a weak acid indicator it is admirably adapted for use in the titration of very weak acids by strong bases, since a very slight excess of $\overset{+}{H}$ ions will destroy the ionization of the indicator. It cannot, however, be used in the titration of weak bases, such as ammonia, since the strongly hydrolyzed salt of the base and the indicator would be formed, and, in consequence, the red colour due to the negative ion would appear long before equivalence had been attained.

EXAMPLES OF BASIC INDICATORS

(a) *Methyl Orange.* Methyl orange is a typical basic indicator. The unionized molecule is yellow and the positive ion

red. Consequently, the addition of an alkali to the methyl orange solution suppresses the slight dissociation of the indicator and the solution turns yellow. If, however, an acid is added to the solution the highly dissociated salt of the acid and the basic methyl orange is formed and the solution becomes red. Since methyl orange is a weak base it cannot be used in the titration of weak acids, as the 'end-point' of the titration would be inaccurate owing to the hydrolysis of the salt of methyl orange and the weak acid formed in the titration. It is, however, suitable for use in the titration of weak bases, such as ammonia, by strong acids.

(b) *Methyl Red* is also a basic indicator, and it is still less basic than methyl orange ; it is, therefore, more suitable than methyl orange for use in the titration of very weak bases by strong acids. Its weak basic nature, however, renders it unsuitable for use in the titration of weak acids owing to the considerable hydrolysis of the salt of the acid and the methyl red formed in the titration.

143. THE DISSOCIATION CONSTANTS OF INDICATORS. Let us take the simple case of an indicator which is a weak acid, and which is dissociated, therefore, only feebly ;

$$HA \rightleftharpoons \overset{+}{H} + \bar{A}.$$
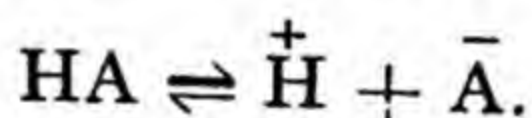
Then, by the Law of Mass Action,

$$\frac{C_H \times C_A}{C_{HA}} = K_I \text{ (Dissociation Constant of the indicator)}.....(3)$$

If we suppose the degree of dissociation of the indicator to be a, and that 1 gram-equivalent of the acid is dissolved in V litres of water, we can obtain from Equation (3) the expression known as *Ostwald's Dilution Law* ; viz. :

$$\frac{\dfrac{a}{V} \times \dfrac{a}{V}}{\dfrac{1-a}{V}} = K_I ;$$

i.e.

$$\frac{a}{(1-a)V} = K_I \dots \dots (4)$$

Now, if one drop of the acid indicator is added to a comparatively large volume of a solution of hydrogen ion concentration C_H, then the alteration in the value of C_H will be practically negligible (since the hydrogen ion concentration

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of the indicator is very small compared with C_H), and it can be treated as if it remained constant.

Then, by the application of Ostwald's Dilution Law (4), Equation (3) becomes

$$\frac{C_H \times \dfrac{a}{V}}{\dfrac{I - a}{V}} = K_I$$

i.e.

$$\frac{a}{I - a} = \frac{K_I}{C_H} \dotfill (5)$$

We have now obtained an expression from which we can calculate the degree of dissociation of an indicator in aqueous solution. In other words, if the dissociation constant of the indicator is known it is possible to predict approximately the concentration of hydrogen ions at which the indicator will give a colour change. To take a special case, it will be seen from Equation (5) that when $a = 0.5$, i.e. when the indicator is 50% ionized, K_I will equal C_H. Thus, the concentration of hydrogen ions in a half neutralized solution is numerically equal to the dissociation constant of the indicator. In consequence, the colour of the indicator used will, at the half-neutralization point, be midway between the colour of the un-ionized molecule and the colour of the ion at the neutralization point. Moreover, if the degree of dissociation of the indicator is very small, the colour will approximate to that of the un-ionized molecule, and, if ionization is practically complete, the colour will be that corresponding to the colour of the ion. We thus arrive at the important conclusion that if we know the dilution of the indicator in any solution we can tell within what limits of hydrogen ion concentration the colour of the indicator changes. For example, methyl orange is light red when $C_H = 10^{-3}$, orange when $C_H = 10^{-4}$, and yellow when $C_H = 10^{-5}$. We conclude, therefore, that the dissociation constant (basic) of methyl orange is 10^{-10} $\left(\text{i.e. } \dfrac{10^{-14}}{10^{-4}}\right)$ (see § 140).

Recent research has revealed that the colour change of an indicator is not due to simple ionization alone, but that it is also due to a tautomeric change in the un-ionized molecules of the indicator. Nevertheless, this does not interfere with the application of the Law of Mass Action to the problem. For example, suppose we have an acid indicator the un-ionized molecules of which exist as an equilibrium mixture of HXO and HOX, the

latter of which ionizes giving a negative ion of the same colour as the un-ionized HOX. HXO is colourless. Then, in aqueous solution, we have

$$HXO \rightleftharpoons HOX \rightleftharpoons \overset{+}{H} + \overset{-}{OX}$$
colourless   coloured   coloured

Then, $\dfrac{C_{HOX}}{C_{HXO}} = k_1$, and $\dfrac{C_H + C_{HOX}}{C_{HOX}} = k_2$.

Consequently, K_I, the dissociation constant of the indicator, will depend upon the magnitudes of k_1 and k_2, and therefore, will obey the Law of Mass Action. The actual value of K_I is $\dfrac{k_1 \times k_2}{1 + k_1}$. We are, thus justified in treating the behaviour of indicators from the simplest case where tautomerism may be neglected.

Similarly, phenolphthalein is colourless at $C_H = 10^{-7}$, feebly coloured at $C_H = 10^{-8}$, and deeply pink at $C_H = 10^{-9}$. Therefore, the dissociation constant of phenolphthalein is in the region of 10^{-8}.

The following table shows the approximate dissociation constants for the common indicators :

| Indicator		K_I
Methyl Orange	..	10^{-10} (basic)
Methyl Red ..	..	10^{-9} (basic)
Paranitrophenol	..	10^{-8}
Litmus ..	..	10^{-7}
Phenolphthalein	..	10^{-9}

It will be readily appreciated that here we have a method of determining the region of hydrogen ion concentrations at which any indicator is effective. For example, methyl orange is effective at a hydrogen ion concentration of $10^{-4}(K_W = 10^{-14})$, and litmus at a hydrogen ion concentration of 10^{-7} gram-equivalents per litre. Thus, litmus is most effective at the neutral point (at $24°$ C.).

144. THE HYDROGEN ION CONCENTRATION OF SALT SOLUTIONS. We have seen that an indicator, in aqueous solution, will give a colour change at a definite concentration of hydrogen ions. In order, therefore, to select a suitable indicator for use in a titration we must know the hydrogen ion concentration of the salt solution formed in the titration.

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(a) *The Salt of a Strong Acid and a Strong Base.* For example, to choose an indicator for the neutralization of HCl by NaOH, we must chose one which has a dissociation constant of the same order as the hydrogen ion concentration of the NaCl solution formed in the titration. Now, we have seen that the concentrations of $\overset{+}{H}$ and $\overset{-}{OH}$ ions in a NaCl solution are equal (§ 9), therefore, since $C_H = C_{OH}$, the solution must be neutral; and in neutral solution, $C_H = 10^{-7}$. Therefore, the indicator chosen for the titration must have a dissociation constant of the same order. This condition is satisfied by litmus, the dissociation constant of which in 10^{-7}, and litmus is the best indicator to use whenever a strong acid is titrated by a strong base.

(b) *The Salt of a Weak Acid and a Strong Base.* Let us consider the case where hydrocyanic acid, HCN (a weak acid), is titrated by KOH (a strong base). As a result of the titration, the salt, KCN, will be formed; this salt will be highly dissociated, and, at the same time, will be strongly hydrolyzed, viz. :

$$KCN \rightleftharpoons \overset{+}{K} + \overset{-}{CN}$$

$$H_2O \rightleftharpoons \overset{-}{OH} \quad \overset{+}{H}$$

$$\Updownarrow$$

$$HCN$$
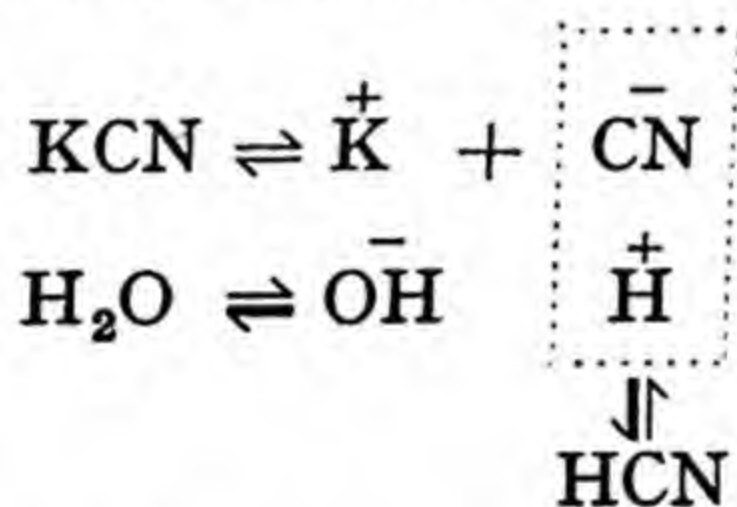
The feebly ionized acid, HCN, is formed, and, in consequence of the removal of $\overset{+}{H}$ ions from the solution, more H_2O molecules will dissociate in order to restore the equilibrium between the un-ionized water and its ions. Thus, there is an excess of $\overset{-}{OH}$ ions in the solution, and an indicator such as litmus, which gives a blue colour with $\overset{-}{OH}$ concentrations above 10^{-7}, will, therefore, give an alkaline reaction with the KCN solution. We have to select, therefore, an indicator which has a dissociation constant of the same order as the hydrogen ion concentration of the KCN solution. Now, although the solution gives an alkaline reaction with litmus, it is electrically neutral. Therefore, the total number of positive ions must equal the total number of negative ions, viz. :

$$C_H + C_K = C_{OH} + C_{CN}.$$

But, owing to hydrolysis, C_H is very small, and can be

neglected in comparison with the other ions. Moreover, C_K and C_{CN} are not equal, since some of the $\overline{CN}$ ions have been removed by hydrolysis to form un-ionized HCN ; but since each $\overline{CN}$ ion that has been removed by hydrolysis has been replaced by a fresh $\overline{OH}$ ion from the water, it follows that the concentration of the HCN formed by hydrolysis is equal to the concentration of the $\overline{OH}$ ions, viz. :

$$C_{HCN} = C_{OH}.$$

From Equation (2), which states that $C_H \times C_{OH} = K_W$, we can arrive at the expression

$$C_{HCN} = \frac{K_W}{C_H} \quad \dots\dots\dots\dots\dots\dots(6)$$

But the HCN is in equilibrium with its ions, so that

$$\frac{C_H \times C_{CN}}{C_{HCN}} = K_A \text{ (the dissociation constant of HCN).}$$

Substituting in this expression the value of C_{HCN} obtained in Equation (6), we have

$$\frac{C_H \times C_{CN}}{\dfrac{K_W}{C_H}} = K_A \; ;$$

and, assuming that the KCN is completely ionized, and neglecting the $\overline{CN}$ ions which have been removed by hydrolysis, we get

$$C_{CN} = \frac{1}{V},$$

where V is the number of litres of solution containing 1 gram-equivalent of KCN.

Substituting this value of C_{CN} in the above expression, we obtain

$$\frac{C_H \times \dfrac{1}{V}}{\dfrac{K_W}{C_H}} = K_A \; ;$$

i.e. $$(C_H)^2 = K_A K_W V$$

Thus, $$C_H = \sqrt{K_A K_W V} \quad \dots\dots\dots\dots(7)$$

We now have an expression by means of which we can calculate the hydrogen ion concentration of a solution of

KCN, and, also, of the solution of any salt of a weak acid and a strong base; e.g.:

To Choose an Indicator for the Titration of Benzoic Acid by Decinormal NaOH. K_A, the dissociation constant of benzoic acid, is $6\cdot7 \times 10^{-5}$. $K_W = 10^{-14}$, and, since the sodium benzoate solution obtained when ' equivalence ' is reached is decinormal, V will equal 10.

Thus,
$$C_H = \sqrt{6\cdot7 \times 10^{-5} \times 10^{-14} \times 10},$$
$$= \sqrt{10^{-17\cdot2}},$$
$$= 10^{-8\cdot6}.$$

Therefore, we must choose an indicator which has a dissociation constant of this order. The indicator which satisfies this condition is phenolphthalein, which has a dissociation constant of 10^{-9}.

(c) *The Salt of Strong Acid and a Weak Base.* Let us consider the case where ammonia solution (a weak base) is titrated by HCl (a strong acid). As a result of the titration the salt ammonium chloride is formed; this salt is strongly ionized, and, at the same time, it is hydrolyzed, viz. :

$$NH_4Cl \rightleftharpoons \overset{+}{NH_4} + \overset{-}{Cl}$$

$$H_2O \rightleftharpoons \overset{-}{OH} + \overset{+}{H}$$
$$\Updownarrow$$
$$NH_4OH$$
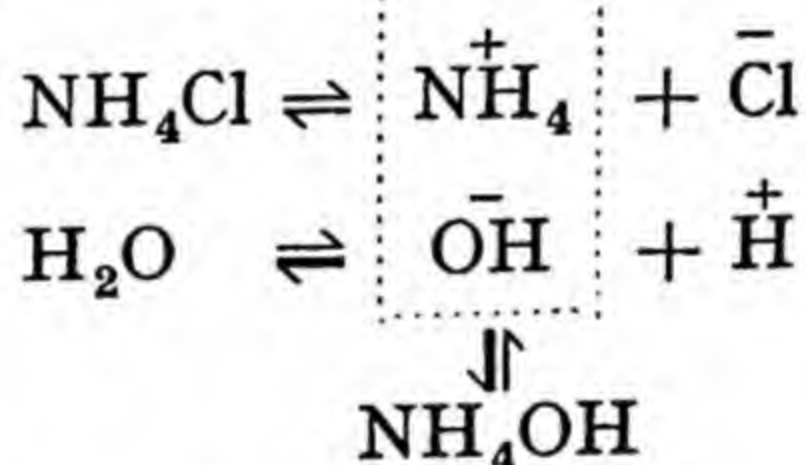
In consequence of the excess of $\overset{+}{H}$ ions the $\overset{+}{H}$ ion concentration will be greater than 10^{-7}, and, therefore, litmus will give an acid reaction with the solution. Here, again, since the solution is electrically neutral, the total number of positive ions must equal the total number of negative ions, viz. :

$$C_H + C_{NH4} = C_{OH} + C_{Cl}.$$

But, owing to hydrolysis, C_{OH} is very small compared with the other concentrations and can be neglected. Moreover, C_{NH4} and C_{Cl} are not equal, since some of the $\overset{+}{NH_4}$ ions have been hydrolyzed to NH_4OH; and, as each $\overset{+}{NH_4}$ ion removed in this way has been replaced by a hydrogen ion, the concentration of the undissociated NH_4OH will be equal to the concentration of the $\overset{+}{H}$ ions, viz. :

$$C_{NH4OH} = C_H.$$

The NH_4OH, however, is in equilibrium with its ions, so that

$$\frac{C_{NH_4} \times C_{OH}}{C_{NH_4OH}} = K_B \text{ (the dissociation constant of the base).}$$

Substituting in this expression the value of C_{NH_4OH} obtained above, we get

$$\frac{C_{NH_4} \times C_{OH}}{C_H} = K_B.$$

But, from Equation (2) $\quad C_{OH} = \dfrac{K_W}{C_H}$

Therefore, $\qquad \dfrac{C_{NH_4} \times \dfrac{K_W}{C_H}}{C_H} = K_B \dots\dots\dots\dots\dots(8)$

and, assuming the NH_4Cl to be completely ionized and neglecting the $\overset{+}{N}H_4$ ions removed by hydrolysis, we have

$$C_{NH_4} = \frac{1}{V},$$

where V is the number of litres of solution containing 1 gram-equivalent of NH_4Cl.

Substituting this value for C_{NH_4} in Equation (8), we get

$$\frac{\dfrac{1}{V} \times \dfrac{K_W}{C_H}}{C_H} = K_B ;$$

i.e. $\qquad (C_H)^2 = \dfrac{K_W}{K_B V}.$

Thus, $\qquad C_H = \sqrt{\dfrac{K_W}{K_B V}} \dots\dots\dots\dots\dots\dots\dots\dots(9)$

We now have an expression by means of which we can calculate the H ion concentration of a solution of ammonium chloride, and, also, of the solution of any salt of a strong acid and a weak base.

For example, the dissociation constant of ammonium hydroxide is $1 \cdot 8 \times 10^{-5}$, so that in a decinormal solution of NH_4Cl

$$C_H = \sqrt{\frac{10^{-14}}{1 \cdot 8 \times 10^{-5} \times 10}}$$
$$= 10^{-5}$$

Then, the best indicator to use in the titration of ammonium hydroxide by HCl (decinormal) is methyl red, since this

indicator has a (basic) dissociation constant of 10^{-9}, which corresponds to a $\overset{+}{H}$ ion concentration of 10^{-5} ($K_W = 10^{-14}$).

(d) *The Salt of a Weak Acid and a Weak Base.* Owing to the very high degree of hydrolysis of such a salt it is practically impossible to obtain accurate results with any indicator ; the $\overset{+}{H}$ ion concentration of the solution does not vary greatly with moderate additions of either acid or base, and it is thus very difficult to obtain a good ' end-point ' in a titration. As, however, there is never any need to titrate a weak acid with a weak base, the subject need not be examined further. A weak acid is always titrated with a strong base, and a weak base with a strong acid.

145. THE FOUR RULES OF TITRATION. From the foregoing considerations we can deduce four simple rules for the choice of an indicator in any titration where normal or decinormal solutions are employed :

(1) Where a strong acid is to be titrated by a strong base, or *vice versâ*, use litmus ; though any indicator may be used in ordinary titration where the limits of experimental error are not very small.

(2) In the titration of a strong acid by a weak base use a strongly acid indicator (*p*-nitrophenol) or a weak basic indicator (methyl red or methyl orange).

(3) In the titration of a weak acid by a strong base choose a weak acid indicator (phenolphthalein).

(4) Never titrate a weak acid with a weak base or *vice versâ*.

Where very accurate titration is desired, the $\overset{+}{H}$ ion concentration of the resulting salt solution must be calculated by either Equations (7) or (9), and an indicator chosen which has a dissociation constant of the same order as the C_H value of the salt solution.

146. THE BEHAVIOUR OF POLYBASIC ACIDS. Considered in the light of our knowledge of the variation of hydrogen ion concentration during titration, the behaviour of polybasic acids towards various indicators becomes intelligible.

(a) *Orthophosphoric Acid.* We have seen (§ 29) that orthophosphoric acid behaves as a monobasic acid when methyl orange is the indicator, and as a dibasic acid if phenolphthalein is employed. The reasons for this are now quite clear :

APPENDIX II—LOGARITHMS—con.

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	5	6	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	5	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	4	5	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	2	3	4	5	6	6	7
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	6	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	6	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	6	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7626	1	1	2	3	4	4	5	6	6
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	6
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	6
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	4	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	4	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	4	4	5	6	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	4	4	5	6	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	4	4	5	6	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	2	3	4	4	5	5
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	2	3	4	4	5	5
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	5
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	5
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	4	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	4	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	4	4	5	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	4	4	5	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5

APPENDIX II—LOGARITHMS—con.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	2
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	2
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	3	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3

APPENDIX II—ANTILOGARITHMS—con.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	3	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	3	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	5	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	7
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8

(The right-hand nine columns are Mean Differences.)

APPENDIX II—ANTILOGARITHMS—con.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	7	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	8	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	6	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	12	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	14
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	10	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	14	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	9	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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